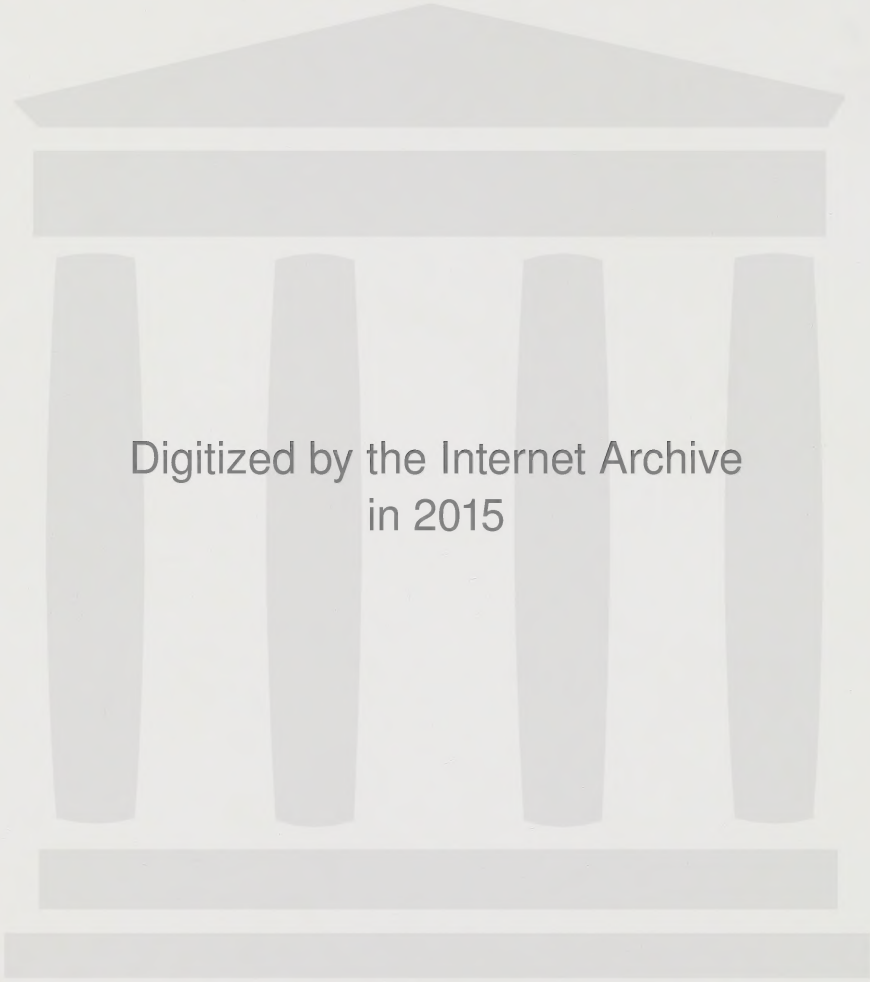
AECV93-R4

Evaluation of Split Sample Survey Results for Pulp and Paper Related Chlorinated Phenolic Compounds

Alberta
ENVIRONMENTAL CENTRE



EVALUATION OF SPLIT SAMPLE SURVEY RESULTS FOR PULP AND PAPER RELATED CHLORINATED PHENOLIC COMPOUNDS

by

C.I. JOHNSON and L.Z. FLORENCE
ALBERTA ENVIRONMENTAL CENTRE
VEGREVILLE, ALBERTA

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ABSTRACT

Sets of split sample pairs of effluents from three Alberta kraft pulp mills were analyzed for pulp and paper related chlorinated phenolic compounds at both the Alberta Environmental Centre (AEC) and at laboratories engaged by the pulp mills. Results were reported to Water Quality Branch of Standards and Approvals Division of Alberta Environment and the two sets of data compared. Concentrations of chlorinated phenols in the effluents reported by the pulp mills were significantly lower than those reported by AEC. Statistical evaluation revealed that results reported by the pulp mills were significantly less precise than those reported by AEC. Results for chlorinated guaiacols followed a similar pattern. Concentrations for all chlorinated guaiacols reported by the pulp mills were significantly lower than those reported by AEC and with the exception of the results for 3,4,5-trichloroguaiacol and 4,5,6-trichloroguaiacol, were significantly less precise. Concentrations of chlorinated catechols reported by the mills were consistent with those reported by AEC but again, with the exception of 4,5-dichlorocatecol, were significantly less precise.

A statistical evaluation of low level results (<2.0 µg/L) showed not only poor precision in the results reported by the pulp mills, but also a real risk of "false negatives" or compounds being reported as "not detected" by the pulp mills when present in samples in concentrations up to twenty times higher than the pulp mills stated detection limits.

1 INTRODUCTION

This report evaluates the quality of results from analysis of kraft pulp mill effluent samples for pulp and paper related chlorinated phenolic compounds (PPCPs) submitted to Alberta Environment (currently, Environmental Protection) by pulp mills. Alberta kraft pulp mills are required to analyze their effluent for PPCPs and submit the results to Alberta Environment on a weekly basis. The pulp mills employ private laboratories to conduct these analyses. At the request of the Water Quality Branch of Standards and Approvals Division of Alberta Environment, a split sample survey, designed to evaluate the accuracy and the precision of the results submitted to Alberta Environment by the pulp mills, was undertaken by the Trace Analysis Program at the Alberta Environmental Centre (AEC). Over the winter and spring of 1992, a total of 20 effluent samples from the three Alberta kraft pulp mills were split and analyzed at AEC as well as the laboratory contracted by the mill. Results of all analyses were submitted to Ian Mackenzie at the Water Quality Branch. The previously documented survey protocol is appended to this report (Appendix A). The results of analyses reported by the mills and AEC, to Water Quality Branch, are listed in Appendix B.

Compounds common to the AEC and pulp mills reports, along with detection limits and suppliers used by AEC, are listed in Table 1. At the time of the survey, no certified standards or certified reference materials were available. For the purposes of assessing accuracy, the AEC results were used as the standard against which the mills' results were evaluated. Results of PPCP sample spiking, conducted as part of the AEC quality control/quality assurance, demonstrate that the AEC results are accurate with respect to the purchased standards (Appendix C).

2 MATERIALS AND METHODS

2.1 Statistical Methods Used to Evaluate Results

Gas chromatography coupled with mass spectrometry (GC/MS) analysis was used to generate both the AEC and mill data. This technique is characterized by constant relative error over the dynamic range of the analytical method (deviations indicate problems with the method) and for the duration of the survey. This property is illustrated by the AEC results presented

below (Figures 2, 4, and 6). In this report log normal distributions, which possess the above properties, are used to approximate the random analytical errors for each compound.

Table 1. Data reporting limits and supplier of standard materials to AEC.

Compound	Detection Limits		Supplier of Standards used by AEC
	Pulp Mills[1]	AEC[2]	
2,4-Dichlorophenol	0.1	0.5	Aldrich Chemical Co., Milwaukee, WI
2,4,6-Trichlorophenol	0.1	0.5	Aldrich Chemical Co., Milwaukee, WI
4,5-Dichloroguaiacol	0.1	0.5	Helix Biotech, Vancouver, BC
4,6-Dichloroguaiacol	0.1	0.5	Helix Biotech, Vancouver, BC
3,4,5-Trichloroguaiacol	0.1	0.5	Helix Biotech, Vancouver, BC
3,4,6-Trichloroguaiacol	0.1	0.5	Helix Biotech, Vancouver, BC
4,5,6-Trichloroguaiacol	0.1	0.5	Helix Biotech, Vancouver, BC
Tetrachloroguaiacol	0.1	0.5	Helix Biotech, Vancouver, BC
3,5-Dichlorocatechol	0.1	0.5	Helix Biotech, Vancouver, BC
4,5-Dichlorocatechol	0.1	0.5	Helix Biotech, Vancouver, BC
3,4,5-Trichlorocatechol	0.1	0.5	Helix Biotech, Vancouver, BC
3,4,6-Trichlorocatechol	0.1	1.0	Helix Biotech, Vancouver, BC
Tetrachlorocatechol	0.1	1.0	Helix Biotech, Vancouver, BC
3,4,5-Trichloroveratrole	0.1	1.0	Helix Biotech, Vancouver, BC
4,5,6-Trichlorosyringol	0.1	1.0	Helix Biotech, Vancouver, BC

[1] Detection limit stated in report.
[2] Method detection limit guaranteed in report. Results below these limits are reported.

Accuracy of the mill results, relative to the AEC results, was evaluated using the general linear model:

Equation 1.

$$Ln \frac{Result_{MILL}}{Result_{AEC}} = T_i + e_{ij}$$

where the T_i's are the mean of the natural logarithms of the i^{th} AEC-Mill ratio for Mills A, B and C plus random error of the i^{th} mill, j^{th} observation. Accuracy was evaluated by testing the null hypothesis:

Equation 2.

$$H_o: \ T_A = T_B = T_C = O$$

The SAS code and results of tests among mills appear in Appendices B, E and F, respectively. A discussion and summary of the results the SAS analysis is presented below.

The precision of the mill results was evaluated using the variances of the replicate and duplicate differences for the compounds analyzed. While the pairs analytical results are highly correlated, the random errors of the analyses are independent and covariance of the error is zero. The variance of the logarithms of the ratio of pairs is simply the sum of the variances of the individual analyses:

$$\sigma^2_{rep.} = \sigma^2_{AEC} + \sigma^2_{Mill}$$

and

$$\sigma^2_{dup.} = \sigma^2_{AEC} + \sigma^2_{AEC}$$

While the null hypothesis $\sigma^2_{Mill} = \sigma^2_{AEC}$ is not easily tested, a related null hypothesis $\sigma^2_{Rep.} \leq \sigma^2_{Dup.}$, can be tested using the F statistic estimated by the ratio of the two sample variances: $s^2_{Rep.}/s^2_{Dup.}$. If $s^2_{Rep.}$ is found to be significantly larger than $s^2_{Dup.}$ it can be concluded the σ^2_{Mill} is greater than σ^2_{AEC} and the mill results are less precise than the AEC results.

2.2 Materials and Laboratory Methods

PPCP analyses at AEC were conducted as described in AEC Method AE130.0 (Appendix D). This method involves *in situ* acetylation/extraction of the PPCPs from effluent and analysis of the derivatized extract by gas chromatography coupled to a mass selective detector (GC/MSD). The MSD is operated in a selected ion monitoring mode, with only ions applicable to the analyte being monitored. Quantification is done using one ion (per compound) while an additional two ions are used to confirm the identification of compounds.

A Hewlett Packard 5970 GC/MSD system with either a PASCAL Chemstation or MS-DOS Chemstation data system was used for the GC/MSD determination. All AEC data has

been corrected for the recovery of surrogate compounds, as requested by Ian MacKenzie of the Water Quality Branch.

PPCP analyses of mill samples by the contractor were also done using GC/MSD but method details and documentation are not available.

Statistical analysis, as described in the survey protocol, was done using PROC GLM of SAS, version 6.08, on a 386DX IBM compatible computer. SAS code and results are appended to this report (Appendices E and F). Microsoft Excel 3.0 and Lotus 123 Version 3.1+ on a 486DX IBM compatible computer were used to produce summary statistics, data plots and linear regressions.

3 RESULTS AND DISCUSSION

The statistical model described in Equation 1 was evaluated by applying SAS Proc GLM to the replicate analysis results. The complete reports are listed in Appendix F and the results are summarized in Table 2. The results indicate that, except for 4,5-dichlorocatechol, there are no significant difference in accuracy among the mills. However, there are significant differences in accuracy between the mills and AEC for several compounds. To increase the power of the analysis, results were pooled and differences between the mills and AEC were evaluated using a paired-t test, the t statistic for each compound is calculated as the average of the natural logarithms of replicate pairs, divided by the standard error of the natural logarithms of replicate pairs. The associated two-tail probabilities (t significantly different than zero) and the sample means and standard errors are listed in Table 3. The mill results for most compounds were significantly lower than those of AEC but whether these differences are of practical importance will have to be decided by the users of the data (note that the mills do not state whether their results have been corrected for recovery).

The comparisons of replicate and AEC duplicate variances are summarized in Table 4. For most compounds, the variance of the natural logarithms of replicate pair ratios is significantly larger than the natural logarithms duplicate pair ratios. This indicates that the mill results are significantly less precise than the AEC results. A more thorough discussion on a compound class basis follows.

Table 2. Summary of SAS Proc GLM evaluation PPCP replicate results.

Compound	Partial Null Hypothesis $T_A = T_B = T_C$	Probability >t of Partial Null Hypothesis		
		$T_A = 0$	$T_B = 0$	$T_C = 0$
2,4-Dichlorophenol	Accept	0.0001	0.0005	0.0001
2,4,6-Trichlorophenol	Accept	0.0263	0.0120	0.0015
4,5-Dichloroguaiacol	Accept	0.1431	0.1866	0.4087
4,6-Dichloroguaiacol	Accept	0.3833	0.7296	0.2967
3,4,5-Trichloroguaiacol	Accept	0.0006	0.0002	0.0004
3,4,6-Trichloroguaiacol	Accept	0.7546	0.4505	0.4836
4,5,6-Trichloroguaiacol	Accept	0.0006	0.1895	0.0011
Tetrachloroguaiacol	Accept	0.0014	0.1445	0.0213
3,5-Dichlorocatechol	Accept	0.6666	0.8664	0.9772
4,5-Dichlorocatechol	Reject	0.0408	0.0001	0.0001
3,4,5-Trichlorocatechol	Accept	0.7546	0.0480	0.5179
Tetrachlorocatechol	Accept	0.8904	NA[1]	0.2085
3,4,5-Trichloroveratrole	Accept	0.1616	0.6067	0.3288

[1] No positive results for this compound in Mill B results.

3.1 Chlorinated Phenols

Only 2,4-dichlorophenol and 2,4,6-trichlorophenol had sufficient data for analysis. Positive results for 2,3,4,6-tetrachlorophenol were frequently reported by AEC, but only one positive result for 2,3,4,6-tetrachlorophenol was reported by the mills. No pentachlorophenol was detected in effluents by either AEC or the mills.

Results for 2,4-dichlorophenol and 2,4,6-trichlorophenol reported by the mills differ significantly from those reported by AEC. Concentrations reported for 2,4-dichlorophenol by pulp mills were, on average, only 38% (Table 3) of those reported by AEC. This may be due to under-recovery of this compound in the mill analysis, caused by losses during concentration steps. Without full documentation of the analytical method used to produce the mill results, this cannot be stated conclusively. Concentrations of 2,4,6-trichlorophenol reported by the mills are

closer to those reported by AEC but were still significantly lower (69%, Table 3). The discrepancy in the results for this compound may be due to the mill results not having been corrected for recovery while AEC results were. Whether this is indeed the case is not known as reports submitted by the mills do not state whether or not the data were corrected for recovery.

Table 3. Summary statistics of log ratio of split sample replicate pairs.

Compound	Average Ln(Mill/AEC)	Standard Deviation	Standard Error	Number of Observations	Probability >T	Mill/AEC
2,4-Dichlorophenol	-0.966	0.297	0.079	14	0.000	38%
2,4,6-Trichlorophenol	-0.372	0.308	0.069	20	0.000	69%
3,4,5-Trichloroveratrole	-0.331	0.511	0.154	11	0.057	72%
4,5-Dichloroguaiacol	-0.209	0.413	0.092	20	0.035	81%
4,6-Dichloroguaiacol	-0.206	1.025	0.342	9	0.564	81%
3,4,5-Trichloroguaiacol	-0.535	0.284	0.065	19	0.000	59%
3,4,6-Trichloroguaiacol	0.299	1.532	0.484	10	0.552	135%
4,5,6-Trichloroguaiacol	-0.553	0.364	0.091	16	0.000	57%
Tetrachloroguaiacol	-0.458	0.397	0.096	17	0.000	63%
3,5-Dichlorocatechol	-0.052	0.851	0.269	10	0.851	95%
4,5-Dichlorocatechol	-0.391	0.301	0.080	14	0.000	68%
3,4,5-Trichlorocatechol	0.033	0.474	0.119	16	0.785	103%
Tetrachlorocatechol	0.113	0.470	0.142	11	0.445	112%

The precision of the concentrations the mills report for the above compounds is significantly less than the results reported by AEC. F-statistics, and probabilities for the split sample replicates and AEC duplicates are given in Table 4. Differences in precision are illustrated in Figures 1 and 2. In Figure 1, the results of the split sample analysis are scattered and consistently fall below the 1:1 correspondence line. However, it should be noted that the scatter of the 2,4,6-trichlorophenol results is appreciably less than that of 2,4-dichlorophenol. Results of the duplicate pairs analyzed at AEC (Figure 2) fall along this line with very little scatter or deviation.

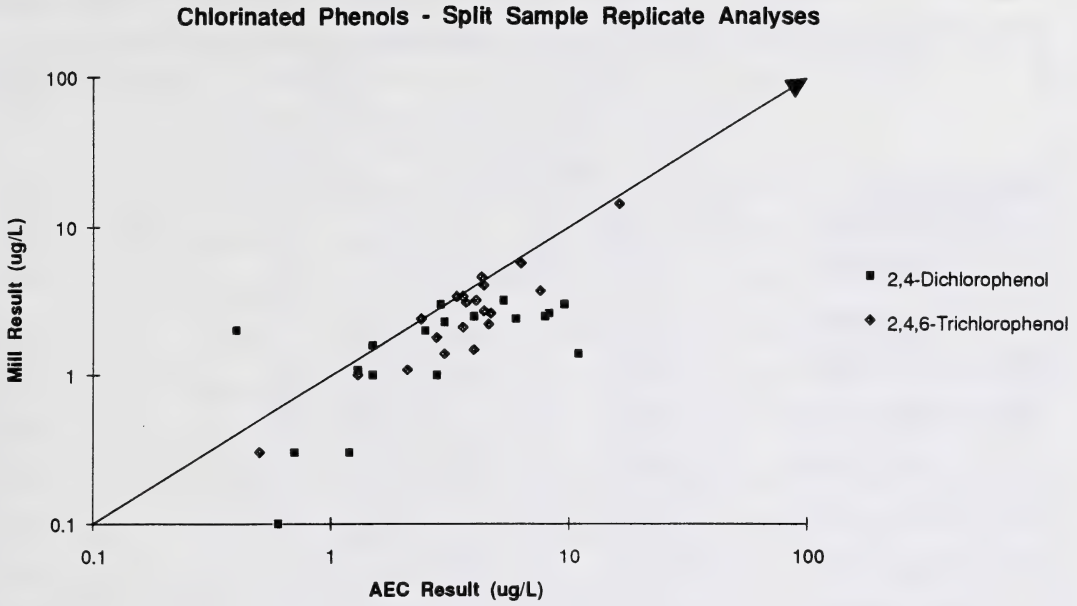

Figure 1. Results of replicate analysis of split samples of bleached kraft mill effluents for chlorinated phenols.

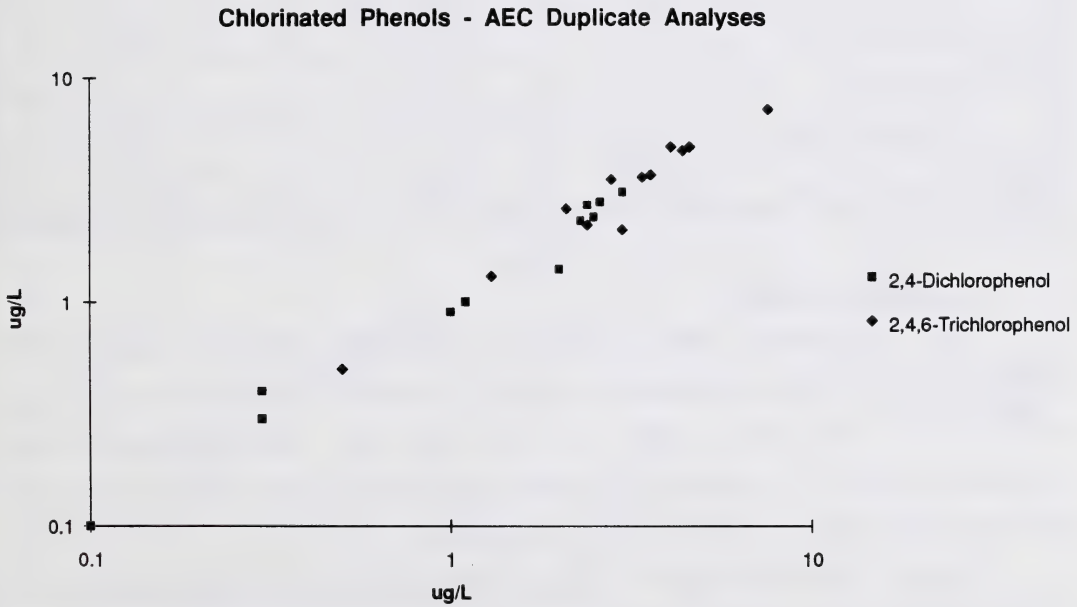

Figure 2. Results of AEC's duplicate analysis of bleached kraft pulp mill effluents for chlorinated phenols.

Table 4. Comparison of variances of split samples replicate pairs and AEC duplicate pairs.

Compound	Split Sample Replicate Pairs		AEC Duplicate Pairs		F Statistic	Probability >F
	Variance	Number of Observations	Variance	Number of Observations		
2,4-Dichlorophenol	0.088	14	0.028	11	3.50	0.034
2,4,6-Trichlorophenol	0.095	20	0.024	12	3.88	0.015
4,5-Dichloroguaiacol	0.171	20	0.047	12	3.63	0.020
4,6-Dichloroguaiacol	1.050	9	0.073	4	14.31	0.030
3,4,5-Trichloroguaiacol	0.081	19	0.070	12	1.16	0.452
3,4,6-Trichloroguaiacol	2.347	10	0.039	10	29.65	0.000
4,5,6-Trichloroguaiacol	0.133	16	0.115	11	1.15	0.466
Tetrachloroguaiacol	0.158	17	0.036	11	4.38	0.014
3,5-Dichlorocatechol	0.725	10	0.103	8	7.05	0.012
4,5-Dichlorocatechol	0.090	14	0.058	11	1.56	0.281
3,4,5-Trichlorocatechol	0.225	16	0.048	9	4.69	0.020
3,4,6-Trichlorocatechol	0.292	4	0.017	3	17.56	0.071
Tetrachlorocatechol	0.221	11	0.021	7	10.31	0.006
3,4,5-Trichloroveratrole	0.261	11	0.037	8	7.02	0.011
4,5,6-Trichlorosyringol	0.326	3	0.021	4	15.74	0.044

3.2 Chlorinated Guaiacols

Again the analytical results submitted by pulp mills differ from those of AEC. Concentrations of chlorinated guaiacol, with the exception of 3,4,6-trichloroguaiacol, are significantly less than those reported by AEC (Table 3). Mean differences between concentrations reported by mills and AEC, which range from 57 to 81% (Table 3), do not differ appreciably from that observed with 2,4,6-trichlorophenol.

Precision of the mill results for 3,4,5-trichloroguaiacol and 4,5,6-trichloroguaiacol does not differ from that of the AEC results (Table 4). The precision of the data submitted for mills for the other chlorinated guaiacols is significantly lower; note Figures 3 and 4 where the scatter of the Mill/AEC replicate pairs about the central line is greater than that of the AEC duplicate

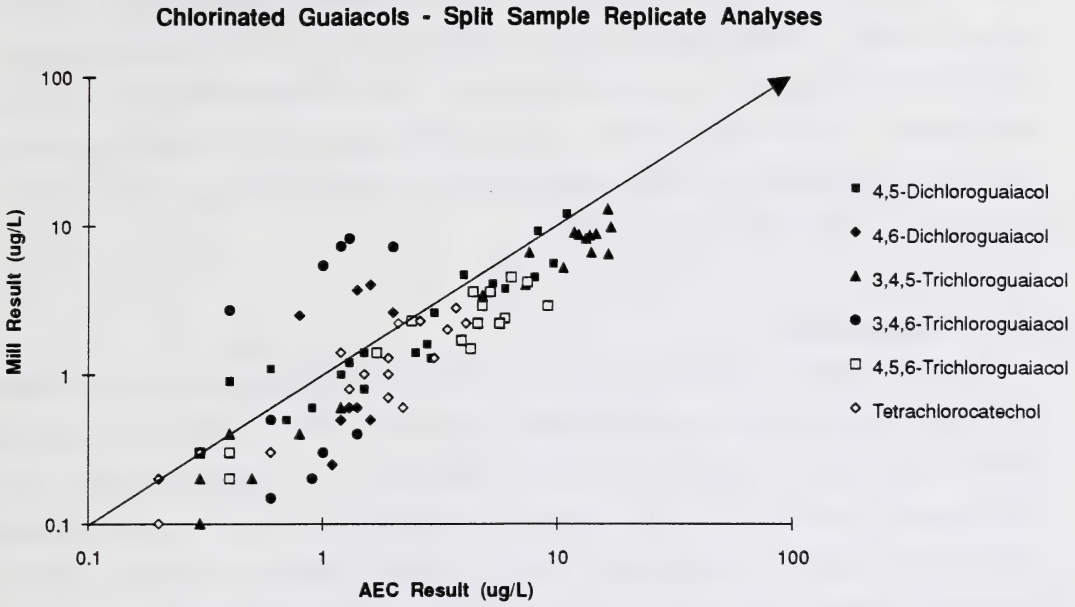

Figure 3. Results of replicate analysis of split samples of bleached kraft mill effluents for chlorinated guaiacols.

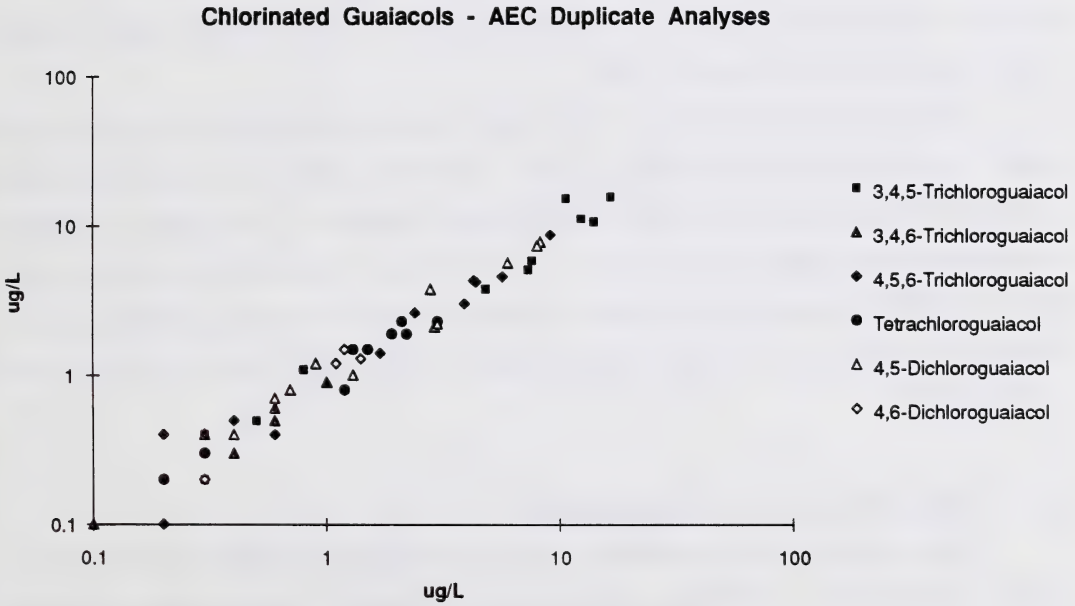

Figure 4. Results of AEC's duplicate analysis of bleached kraft pulp mill effluents for chlorinated guaiacols.

pairs. Also apparent in Figure 3 are five 3,4,6-trichloroguaiacol data pairs which lie well above the rest of the data. These points are probably outliers resulting from: (1) reporting error due to a misplaced decimal point in the analysis reports, or (2) use of misidentified peaks to calculate concentrations. The very large variance in the log differences of replicate pairs supports the hypothesis of reporting errors and suggests a reason for the significantly larger concentrations of this compound in the mill submitted data.

3.3 Chlorocatechols

With exception of 4,5-dichlorocatechol, concentrations of chlorinated catechols reported by the pulp mills are more consistent with those reported by AEC than results for chlorinated guaiacols and phenols. The mills reported concentrations for 3,5-dichlorocatechol, 3,4,5-trichlorocatechol and tetrachlorocatechol which do not differ significantly from those reported at AEC (results in Table 3). The precision of the mill results for these compounds is significantly less as shown by the variances and F-statistics in Table 4. However, when viewing the results for 3,4,5-trichlorocatechol in Figure 5, it is apparent that there is only one point (arrow) which deviates substantially from the 1:1 correspondence line. If this datum is eliminated from the statistical analysis the precision of the remaining results for this compound does not differ significantly between AEC and the mills.

Figure 5 demonstrates there is a very high correlation among the chlorinated catechol results when the concentration exceeds 2 µg/L. Result pairs below this concentration exhibit considerable scatter, not present in AEC duplicate pairs (Figure 6). This suggests a decrease in the reliability of the mill results at these low levels. This may explain the good precision of the mill results for 4,5-dichlorocatechol and 3,4,5-trichlorocatechol which are generally present in effluents in relatively high (>2µg/L) concentrations and the others which are found in lower concentrations.

3.4 Chloroveratroles and Trichlorolsyringol

Chlorinated veratroles and trichlorosyringol were observed in effluent less frequently and in low concentrations. Sufficient positive results for statistical analysis were available for trichloroveratrole and trichlorosyringol. Both these compounds were "under recovered" in the

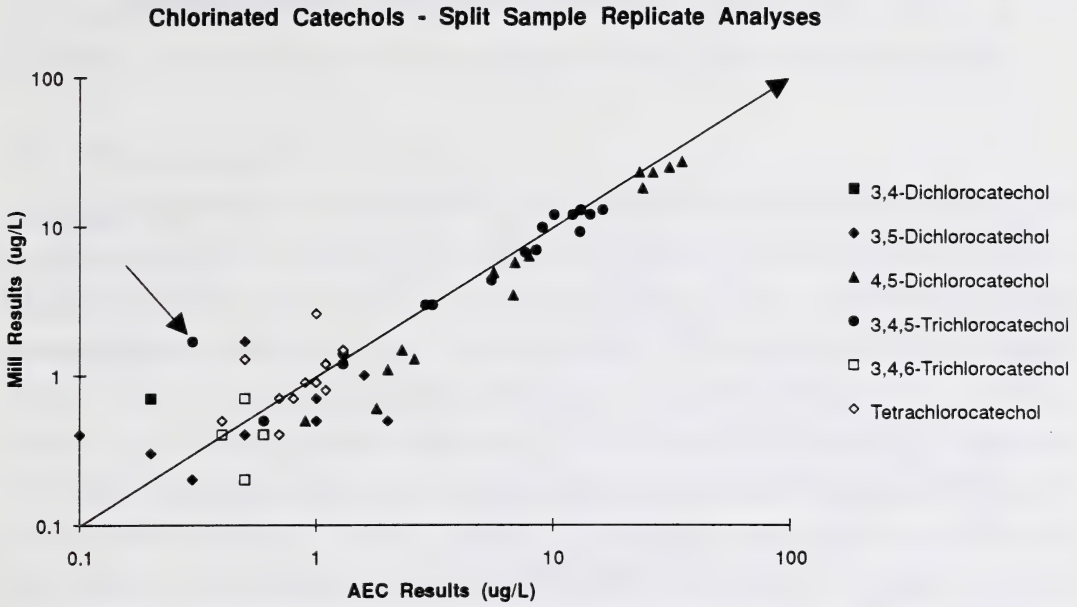

Figure 5. Results of replicate analysis of split samples of bleached kraft mill effluents for chlorinated catechols (see text regarding arrow).

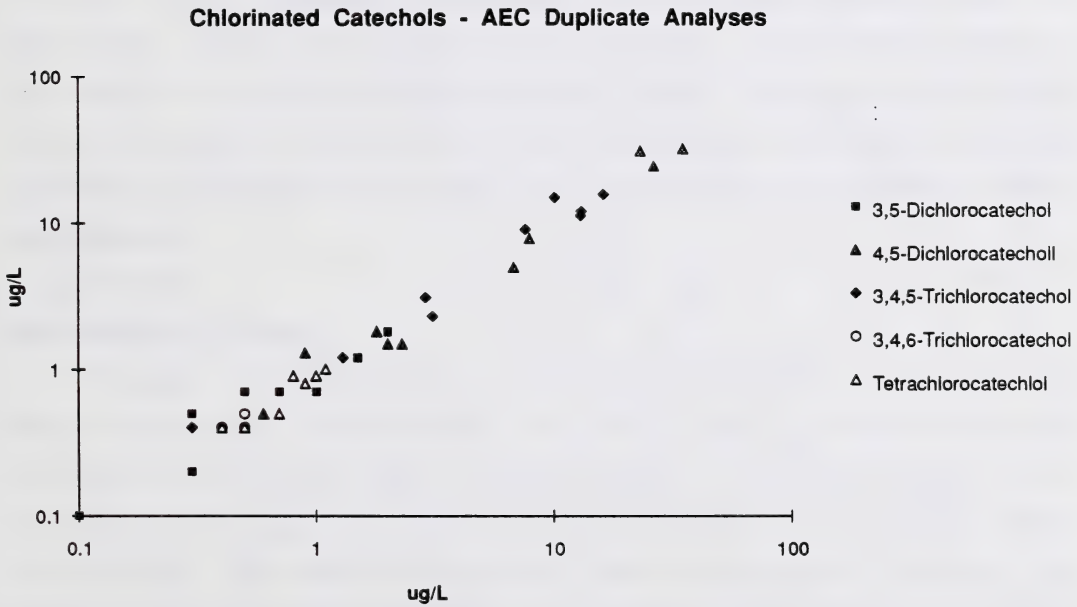

Figure 6. Results of AEC's duplicate analysis of bleached kraft pulp mill effluents for chlorinated catechols.

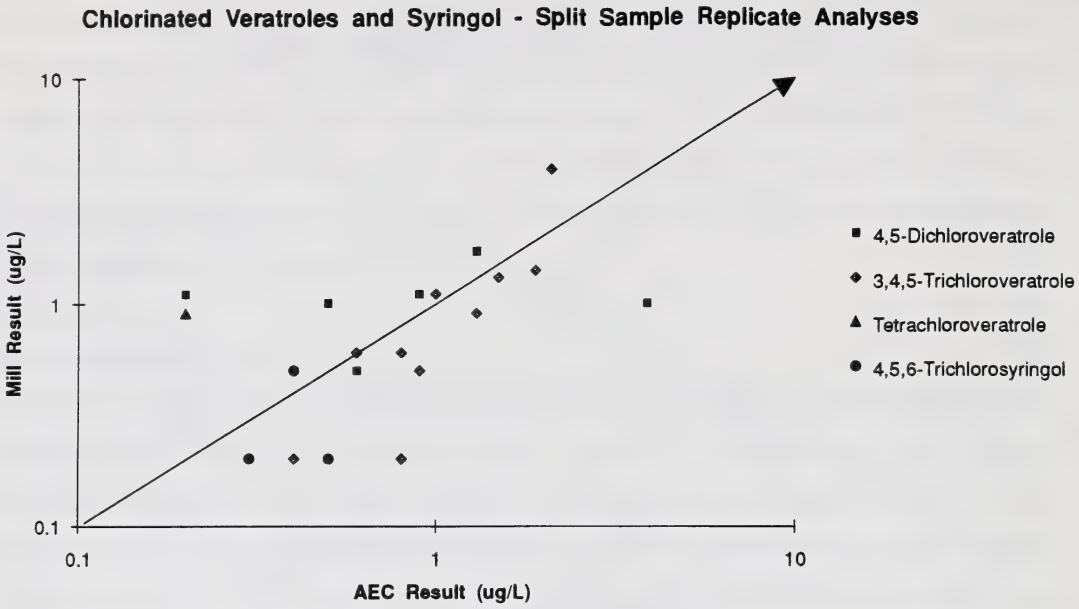

Figure 7. Results of replicate analysis of split samples of bleached kraft mill effluents for chlorinated veratroles and 4,5,6-trichlorosyringol.

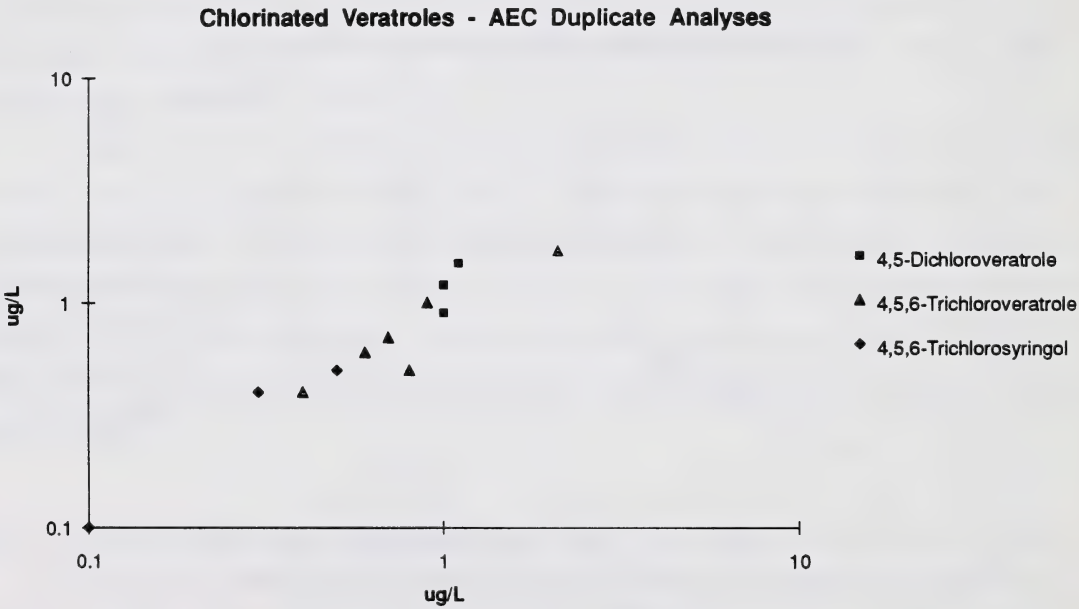

Figure 8. Results of AEC's duplicate analysis of bleached kraft mill effluents for chlorinated veratroles and 4,5,6-trichlorosyringol.

mill results, as compared to AEC results, and the mill results are less precise. This is apparent in Figures 7 and 8 showing plots of split sample replicate and AEC duplicate result pairs.

3.5 False Negative Results

In this report, the term "missing data" refers to concentrations of analytes reported by one source as "not detected" while positive concentrations are reported by the other source for the same sample. This can be due to the reporting of false negative or false positive results. Because of the rigorous criteria used to confirm the identity of compounds, the former is assumed to be the case. The frequency of missing data versus the concentration reported are plotted in Figures 9 and 10 for both mill and AEC results. In both cases, it can be seen that the frequency of missing data decreases with increasing concentration reported by the other source. This agrees with the intuitive assessment that the probability of reporting a false negative increases as the concentration of the analyte decreases. What is striking is that there is a significant frequency for missing data in the mill reported results at 2 µg/L while missing results in the AEC data do not extend past 1.25 µg/L. Careful review of the data (Appendix D) suggests the missing results at 1.00 and 1.25 µg/L may be due to false positives in the mill results and not false negative in AEC results. The mill results causing these false negatives deviate from the patterns of concentration of all compounds observed in the other samples. This pattern of missing data in the mill results, coupled with the scatter observed in replicate results below 2 µg/L, suggest that mill results of concentrations below 2.0 µg/L lack the precision of the AEC results and may not be reliable.

3.6 Stability of Variance

Throughout this discussion, the log variances of random analytical error have been assumed to be the case. Plots of the AEC duplicate pairs (Figures 2, 4, 6, and 8) demonstrate this to be the case for the AEC analytical results but the plots of the replicate results indicate a large increase in the random error in mill results for samples where the concentration of analyte is below 2.0 µg/L. This means that the precision of the mill results above 2.0 µg/L have been considerably understated while the precision of results below 2.0 µg/L is actually worse than the above evaluation indicates. Plots of replicate pairs (Figures 1, 3, 5, and 7) illustrate that the precision of the mill data above 2.0 µg/L is comparable to the precision of AEC data.

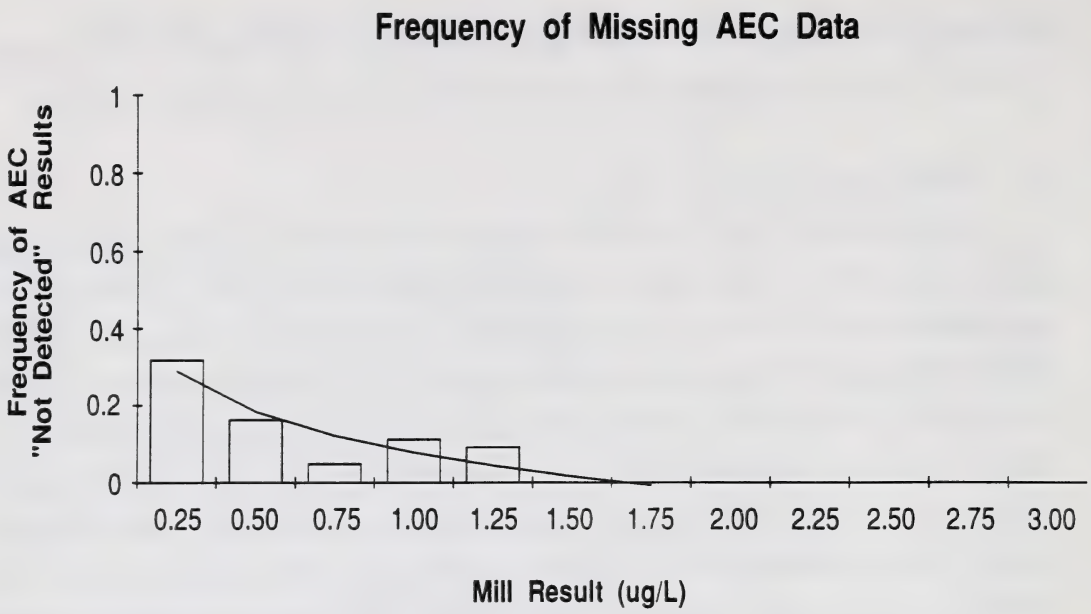

Figure 9. Frequency of missing data in AEC results.

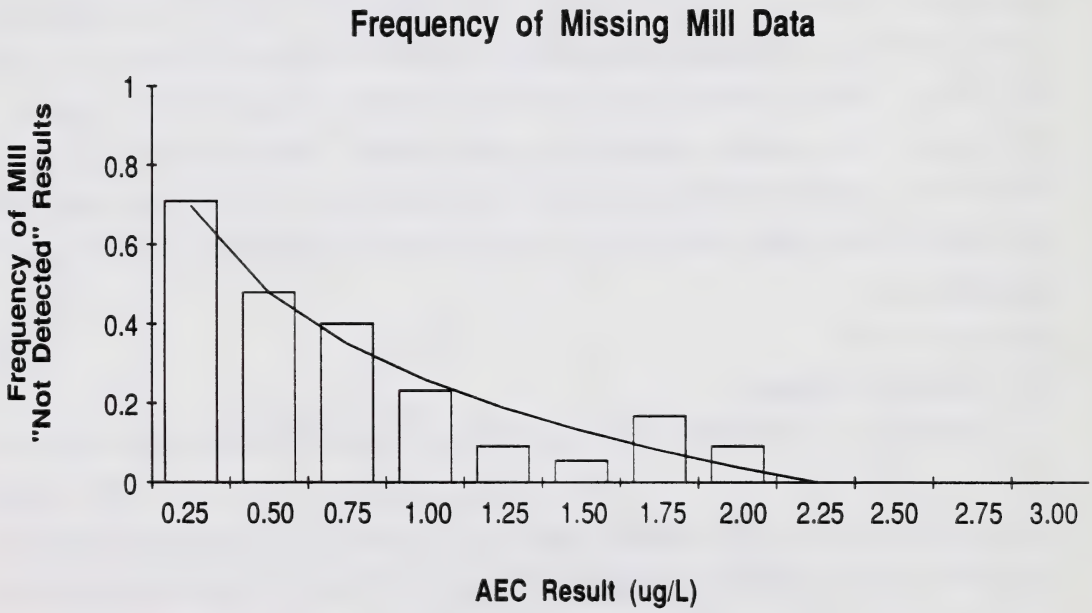

Figure 10. Frequency of missing data in mill results.

4 CONCLUSIONS

Concentrations of chlorinated phenols, guaiacols, veratroles, and syringols reported by the pulp mills are, on average, only 70% of that reported by AEC. Concentrations of chlorinated catechols reported by the mills are comparable to those reported by AEC. AEC results were corrected for recovery but it is not clear if the mill results were corrected. Further assessment of the accuracy of the mill results cannot be made until thorough documentation of the analytical and reporting protocols employed by the mills is made available.

Precision of the results reported by the mills exceeding 2 µg/L, is comparable to those reported by AEC, indicating equivalent results in this concentration range and no appreciable sampling error. However, the precision of results reported by the mills of less than or equal 2 µg/L is significantly less than those of AEC. Furthermore, investigation of missing data, in particular the "not detected" results reported by mills, reveals that when the concentration of analytes is less than or equal 2 µg/L the results from the mills are not reliable and "false negatives" become more likely reported for concentrations up to 20 times the detection limit.

APPENDIX A

PROTOCOL FOR PPCP SPLIT SAMPLE SURVEY

Split Sample Survey Protocol for the Evaluation of Mill Submitted Organochlorine Data

1. Background

Standards and Approvals Division (SAD), Water Quality Branch has requested the Research and Methods Development Branch (R&MDB) to design and conduct a "split sample survey" to evaluate the consistency Adsorbable Organic Halide (AOX) and Pulp and Paper related Chlorophenolics (PPCPs) data provided by the three Alberta kraft pulp mills and the R&MDB.

2. Objectives

This survey is designed to identify any systematic differences in the accuracy and precision of the PPCP and AOX measurements of effluents provided by the R&MDB and those provided by kraft pulp mills. The sensitivity of the method used to generate the data will be evaluated if necessary.

3. Chlorinated Phenols, Guaiacols, and Catechols

This portion of the survey is designed to test two null hypotheses for each parameter included in the PPCP analysis. These null hypotheses are:

Null Hypothesis 1.

H_0: There is no discernible difference in the accuracy of both sets (split) of data.

Null Hypothesis 2.

H_0: There is no discernible difference in the precision of both sets (split) of data.

Statistical Model:

The statistical model with which hypotheses are evaluated (equation 1) is based on the assumption that the results of PPCP analyses are log-normally distributed random variables. This assumption is generally valid for this type of chemical analysis.

If the above assumption is accepted, it follows that the difference of the logs of the sets of data from the split samples, i.e. the logs of the ratios of the two sets of data, are normally distributed random variables which can be described by the following relationship:

$$y=\beta_0+\beta_1 A+\beta_2 B+\beta_3 C+\epsilon \qquad (1)$$

where y is the log ratio of results from the two sets of data, β_0 is the overall mean of the log of the ratio of the results, β_1 is the average of log of the ratio of the two sets of results pertaining to Mill A, β_2 is the average of the log of the ratio of the two sets of results pertaining to Mill B, β_3 is the average of the log of the ratio of the two sets of results pertaining to Mill C, and ϵ is the analytical error. Null hypothesis 1 will be tested using the equality:

$$\beta_0=\beta_1=\beta_2=\beta_3=0$$

within experimental error (an α yet to be chosen). If H_0 fails, sources of error within and among mills will be examined following consultations with the Biometrics Section, AEC. Null hypothesis 2 will be tested using the equality:

$$S^2_{survey}=S^2_{duplicates}$$

where s^2_{survey} is the survey variance estimated using the mean square error and $s^2_{duplicate}$ is the variance of the analysis performed by the R&MDB, estimated from the results of duplicate analyses.

Experimental Design:

Split samples of all weekly effluent samples taken, at each of the three mills, over a three month period, will be collected. Of these, 4 sets (a set being the samples collected at during one week, one sample from each mill) will be selected and analyzed using AEC Method AE130.0. Only after the 4 sets of samples have been analyzed and the results reported to SAD will results, submitted by the mills to SAD, be forwarded to AEC for evaluation using the statistical model described above. If the results of the statistical analysis are inconclusive an additional two sets of samples will be analyzed and the results of the large set of data will be evaluated. It is important that the analysts and the evaluator at the R&MDB be blind to the mill results submitted to SAD until the analysis of samples is complete. The design, including extra sets of samples if required, is shown in Table 1.

Power Analysis:

Power of design has not been evaluated as of this date (920206).

Table 1 Experimental design and "treatment" groups.

Analysis Set	Mill A (Weldwood)	Mill B (P&G)	Mill C (Daishowa)	n
1	1	0	0	1
1	0	1	0	1
1	0	0	1	1
2	1	0	0	2
2	0	1	0	2
2	0	0	1	2
3	1	0	0	1
3	0	1	0	1
3	0	0	1	1
4	1	0	0	2
4	0	1	0	2
4	0	0	1	2
5	1	0	0	2
5	0	1	0	2
5	0	0	1	2
6	1	0	0	1
6	0	1	0	1
6	0	0	1	1

4. Adsorbable Organic Halide (AOX)

This portion of the survey is designed to test two null hypotheses for the two sets of AOX results. These null hypotheses are:

Null Hypothesis 1.

H_0: There is no discernible difference in the accuracy of AOX results reported by mills and those generated at the R&MDB.

Null Hypothesis 2.

H_0: There is no discernible difference in the precision of AOX results reported by mills and those generated at the R&MDB.

All AOX samples submitted will be analyzed and rather than pooling the results from all mills and using a general model, the results from each mill will be evaluated separately.

Statistical Model:

Results will be evaluated by linear regression of each mill[1] reported results (dependent variable) against results generated at the R&MDB (independent variable). Slopes, intercepts, and associated errors resulting from the regressions will be used to test the first null hypothesis as: slope = 1; and intercept = 0.

Hypothesis 2 will be tested by comparing the variance estimated from the difference in results of the split samples and the variance in the R&MDB results estimated from duplicate analyses run in the course of routine AOX analysis.

Confidence levels at which these hypotheses are to be tested shall be ≤ 0.10.

Experimental Design:

Split samples taken at weekly intervals over a three month period will be analyzed for AOX following AEC Method E128.0. Only after the completion of all analysis will the results be compared to those submitted to SAD.

Power Analysis:

Power of this portion of the survey has not been evaluated at this data (920206).

APPENDIX B

PPCP REPLICATE AND DUPLICATE RESULTS

Split Sample Results

Source	Set	Lab	Date	24_DCP[1]	246_T3CP[2]	45_DCG[3]	46_DCG[4]	345_T3CG[5]
				ug/L	ug/L	ug/L	ug/L	ug/L
Mill 11		A	11-Feb	0.7	5.7	12.0	4.0	9.0
Mill 12		A	25-Feb	1.3	2.7	9.3	3.7	8.7
Mill 13		A	03-Mar	1.1	2.6	5.6	0.6	8.8
Mill 14		A	10-Mar	0.6	2.1	4.5	0.5	5.2
Mill 15		A	18-Mar	1.1	3.4	3.8	0.3	6.6
Mill 16		A	24-Mar	1.0	3.1	4.1	0.5	8.2
Mill 21		A	11-Feb		4.6	1.4		9.8
Mill 22		A	20-Feb	0.5	1.0	1.2		3.4
Mill 23		A	24-Feb	0.6	1.5	4.7	2.5	13.0
Mill 24		A	03-Mar	0.9	2.2	1.3	1.2	6.5
Mill 25		A	09-Mar	0.8	1.4	2.6	0.3	4.0
Mill 26		A	16-Mar		0.3	0.5		0.4
Mill 27		A	23-Mar	1.1	2.4	0.9	0.1	6.6
Mill 31		A	10-Feb	0.6	14.0	1.4	2.6	8.6
Mill 32		A	25-Feb		3.7	1.1	0.9	0.2
Mill 33		A	03-Mar		4.0	1.0		
Mill 34		A	11-Mar		1.1	0.6		0.1
Mill 35		A	17-Mar	0.3	1.8	1.6		0.2
Mill 36		A	24-Mar	0.6	3.4	0.8	0.6	0.4
Mill 37		A	31-Mar		3.2	0.5		0.6
Mill 11		B	11-Feb	1.4	6.3	11.0	1.6	11.8
Mill 12		B	25-Feb	2.6	4.4	8.3	1.4	12.4
Mill 13		B	03-Mar	3.0	4.7	9.6	1.4	14.7
Mill 14		B	10-Mar	2.5	3.6	8.0	1.2	10.6
Mill 15		B	17-Mar	2.4	3.4	6.0	1.1	14.0
Mill 16		B	24-Mar	3.2	3.7	5.3	1.6	13.3
Mill 21		B	11-Feb	2.0	4.3	2.5	0.6	16.9
Mill 22		B	20-Feb	1.1	1.3	1.3	0.3	4.8
Mill 23		B	24-Feb	2.5	4.0	4.0	0.8	16.5
Mill 24		B	02-Mar	3.0	4.6	2.9		16.6
Mill 25		B	09-Mar	2.3	3.0	3.0		7.3
Mill 26		B	16-Mar	0.3	0.5	0.7		0.8
Mill 27		B	24-Mar	2.0	2.4	0.4		7.6
Mill 31		B	10-Feb	1.6	16.4	1.5	2.0	13.8
Mill 32		B	26-Feb	0.1	7.6	0.6		0.3
Mill 33		B	03-Mar	0.3	4.4	1.2		0.2
Mill 34		B	11-Mar		2.1	0.9		0.3
Mill 35		B	17-Mar	1.0	2.8	2.8	0.5	0.5
Mill 36		B	25-Mar	1.0	3.6	1.5	1.3	0.4
Mill 37		B	31-Mar	0.3	4.1	0.7	0.0	1.2

[1] 2,4-Dichlorophenol, [2] 2,4,6-Trichlorophenol, [3] 4,5-Dichloroguaiacol, [4] 4,6-Dichloroguaiacol, [5] 3,4,5-Trichloroguaiacol

Split Sample Results

Source	Set	Lab	Date	346_T3CG[6]	456_T3CG[7]	T4CG[8]	34_DCC[9]	35_DCC[10]
				ug/L	ug/L	ug/L	ug/L	ug/L
Mill 11		A	11-Feb	7.3	3.6	2.3		
Mill 12		A	25-Feb		3.6	1.0		
Mill 13		A	03-Mar		2.4	1.0		1.0
Mill 14		A	10-Mar		1.5	0.6		0.5
Mill 15		A	18-Mar	0.2	2.2	1.3		1.7
Mill 16		A	24-Mar	0.3	2.9	0.7		0.4
Mill 21		A	11-Feb	8.2	2.2	2.2		
Mill 22		A	20-Feb	2.7	1.4	1.4		
Mill 23		A	24-Feb	0.4	4.5	2.8		
Mill 24		A	03-Mar	5.4	2.9	1.3		0.7
Mill 25		A	09-Mar	0.2	1.7	0.8	0.4	0.7
Mill 26		A	16-Mar		0.2	0.1		
Mill 27		A	23-Mar	0.5	2.3	2.2	0.1	0.3
Mill 31		A	10-Feb	7.2	4.2	2.0		
Mill 32		A	25-Feb			0.2	0.7	0.4
Mill 33		A	03-Mar				1.0	
Mill 34		A	11-Mar					0.2
Mill 35		A	17-Mar				0.2	0.2
Mill 36		A	24-Mar	0.1	0.3	0.3		0.5
Mill 37		A	31-Mar		0.3	0.3		0.2
Mill 11		B	11-Feb	1.2	5.2	2.6	0.1	0.5
Mill 12		B	25-Feb	1.0	4.4	1.5	0.2	1.5
Mill 13		B	03-Mar	0.9	6.0	1.9		1.6
Mill 14		B	10-Mar	0.6	4.3	2.2		2.0
Mill 15		B	17-Mar	0.9	5.7	1.9		0.5
Mill 16		B	24-Mar	1.0	4.8	1.9		0.5
Mill 21		B	11-Feb	1.3	4.6	4.1	0.1	0.3
Mill 22		B	20-Feb	0.4	1.7	1.2	0.4	0.3
Mill 23		B	24-Feb	1.4	6.4	3.7		0.6
Mill 24		B	02-Mar	1.0	9.1	3.0		1.0
Mill 25		B	09-Mar	0.6	3.9	1.3		0.7
Mill 26		B	16-Mar	0.1	0.4	0.2		0.1
Mill 27		B	24-Mar	0.6	2.4	2.1		0.2
Mill 31		B	10-Feb	2.0	7.5	3.4	0.1	0.3
Mill 32		B	26-Feb	0.3	0.2	0.2	0.2	0.1
Mill 33		B	03-Mar					0.4
Mill 34		B	11-Mar					
Mill 35		B	17-Mar		0.2	0.3		0.3
Mill 36		B	25-Mar		0.3	0.3		1.0
Mill 37		B	31-Mar	0.2	0.4	0.6		

[6] 3,4,6-Trichloroguaiacol, [7] 4,5,6-Trichloroguaiaicol, [8] Tetrachloroguaiacol, [9] 3,4-Dichlorocatechol, [10] 3,5-Dichlorocatechol

Split Sample Results

Source	Set	Lab	Date	45_DCC [11]	345_T3CC [12]	346_T3CC [13]	T4CC [14]	45_DCV [15]
				ug/L	ug/L	ug/L	ug/L	ug/L
Mill 11	A		11-Feb	5.0	9.9		2.6	
Mill 12	A		25-Feb	27.0	13.0	0.7	0.9	
Mill 13	A		03-Mar	25.0	12.0	0.4	0.8	
Mill 14	A		10-Mar	23.0	13.0	0.2	0.7	
Mill 15	A		18-Mar	23.0	12.0	0.4	0.9	
Mill 16	A		24-Mar	18.0	7.0		0.4	0.4
Mill 21	A		11-Feb		4.4			
Mill 22	A		20-Feb	1.5	3.0		1.3	
Mill 23	A		24-Feb	5.8	12.0		1.5	
Mill 24	A		03-Mar	6.4	9.3		1.2	
Mill 25	A		09-Mar	3.5	6.8		0.7	
Mill 26	A		16-Mar	0.5	1.2		0.3	
Mill 27	A		23-Mar	1.1	3.0		0.5	
Mill 31	A		10-Feb		1.4			
Mill 32	A		25-Feb		1.7		0.3	
Mill 33	A		03-Mar					
Mill 34	A		11-Mar			0.1		
Mill 35	A		17-Mar	0.6				
Mill 36	A		24-Mar	1.3	0.5			
Mill 37	A		31-Mar		0.3			
Mill 11	B		11-Feb	5.6	9.0	0.2	1.0	1.7
Mill 12	B		25-Feb	35.0	13.1	0.5	1.0	1.0
Mill 13	B		03-Mar	31.0	14.4	0.6	1.1	0.5
Mill 14	B		10-Mar	23.2	16.2	0.5	0.8	1.1
Mill 15	B		17-Mar	26.4	10.1	0.4	0.9	1.0
Mill 16	B		24-Mar	24.0	8.5	0.2	0.7	1.1
Mill 21	B		11-Feb	3.2	5.5		0.6	
Mill 22	B		20-Feb	2.3	3.1		0.5	
Mill 23	B		24-Feb	6.9	12.1	0.1	1.3	
Mill 24	B		02-Mar	7.9	13.0	0.0	1.1	
Mill 25	B		09-Mar	6.8	7.6	0.2	0.7	
Mill 26	B		16-Mar	0.9	1.3		0.0	
Mill 27	B		24-Mar	2.0	2.9		0.4	
Mill 31	B		10-Feb	0.9	1.3		0.3	
Mill 32	B		26-Feb	0.6	0.3			
Mill 33	B		03-Mar	0.6				
Mill 34	B		11-Mar	0.6				0.3
Mill 35	B		17-Mar	1.8	0.5			0.5
Mill 36	B		25-Mar	2.6	0.6			
Mill 37	B		31-Mar	0.4				

[11] 4,5-Dichlorocatechol, [12] 3,4,5-Trichlorocatechol, [13] 3,4,6-Trichlorocatechol,
[14] Tetrachlorocatechol, [15] 4,5-Dichloroveratrole

Source	Set	Lab	Date	345_T3CV[16] ug/L	T4CV[17] ug/L	456_T3CS[18] ug/L
Mill 11		A	11-Feb	1.3		
Mill 12		A	25-Feb	3.9	0.9	
Mill 13		A	03-Mar	0.6	0.6	
Mill 14		A	10-Mar	0.2		
Mill 15		A	18-Mar	0.5	0.4	
Mill 16		A	24-Mar	0.9		
Mill 21		A	11-Feb			
Mill 22		A	20-Feb			
Mill 23		A	24-Feb	1.1		
Mill 24		A	03-Mar			
Mill 25		A	09-Mar	0.5		
Mill 26		A	16-Mar	0.2		
Mill 27		A	23-Mar	0.6		
Mill 31		A	10-Feb	1.4		
Mill 32		A	25-Feb			0.2
Mill 33		A	03-Mar			
Mill 34		A	11-Mar			
Mill 35		A	17-Mar			0.2
Mill 36		A	24-Mar			0.5
Mill 37		A	31-Mar			
Mill 11		B	11-Feb	1.5	0.1	
Mill 12		B	25-Feb	2.1	0.2	0.1
Mill 13		B	03-Mar	0.8		
Mill 14		B	10-Mar	0.8		
Mill 15		B	17-Mar	0.9		0.1
Mill 16		B	24-Mar	1.3	0.2	0.1
Mill 21		B	11-Feb	0.8		
Mill 22		B	20-Feb	0.4		
Mill 23		B	24-Feb	1.0		
Mill 24		B	02-Mar	0.7		
Mill 25		B	09-Mar	0.9		
Mill 26		B	16-Mar	0.4		
Mill 27		B	24-Mar	0.6		
Mill 31		B	10-Feb	1.9	0.3	0.1
Mill 32		B	26-Feb			0.3
Mill 33		B	03-Mar			0.5
Mill 34		B	11-Mar			
Mill 35		B	17-Mar			0.5
Mill 36		B	25-Mar			0.4
Mill 37		B	31-Mar			0.1

[16] 3,4,5-Trichloroveratrole, [17] Tetrachloroveratrole, [18] 4,5,6-Trichlorosyringol

PPCP Duplicate Analysis Results

Source	Set	Date	Duplicate	24_DCP ug/L	246_T3CP ug/L	45_DCG ug/L	46_DCG ug/L	345_T3CG ug/L
Mill A	2a	02/25/92		2.6	4.4	8.3	1.4	12.4
Mill A	2b	02/25/92	D	2.8	4.7	7.8	1.3	11.2
Mill A	4a	03/10/92		2.5	3.6	8.0	1.2	10.6
Mill A	4b	03/10/92	D	2.4	3.7	7.4	1.5	15.2
Mill A	5a	03/17/92		2.4	3.4	6.0	1.1	14.0
Mill A	5b	03/17/92	D	2.7	3.6	5.7	1.2	10.7
Mill B	2a	02/20/92		1.1	1.3	1.3	0.3	4.8
Mill B	2b	02/20/92	D	1.0	1.3	1.0	0.2	3.8
Mill B	4a	03/02/92		3.0	4.6	2.9		16.6
Mill B	4b	03/02/92	D	3.1	4.9	2.1		15.7
Mill B	5a	03/09/92		2.3	3.0	3.0		7.3
Mill B	5b	03/09/92	D	2.3	2.1	2.2	0.6	5.1
Mill B	6a	03/16/92		0.3	0.5	0.7		0.8
Mill B	6b	03/16/92	D	0.4	0.5	0.8		1.1
Mill B	7a	03/24/92		2.0	2.4	0.4		7.6
Mill B	7b	03/24/92	D	1.4	2.2	0.4		5.9
Mill C	2a	02/26/92		0.1	7.6	0.6		0.3
Mill C	2b	02/26/92	D	0.1	7.2	0.7		0.2
Mill C	4a	03/11/92			2.1	0.9		0.3
Mill C	4b	03/11/92	D		2.6	1.2		0.4
Mill C	5a	03/17/92		1.0	2.8	2.8	0.5	0.5
Mill C	5b	03/17/92	D	0.9	3.5	3.8		0.5
Mill C	7a	03/31/92		0.3	4.1	0.7		1.2
Mill C	7b	03/31/92	D	0.3	4.9	0.8		1.1

PPCP Duplicate Analysis Results

Source	Set	Date	Duplicate	346_T3CG ug/L	456_T3CG ug/L	T4CG ug/L	4_CC ug/L	34_DCC ug/L
Mill A	2a	02/25/92		1.0	4.4	1.5		0.2
Mill A	2b	02/25/92	D	0.9	4.2	1.5	0.2	0.1
Mill A	4a	03/10/92		0.6	4.3	2.2		
Mill A	4b	03/10/92	D	0.7	4.3	1.9	0.3	
Mill A	5a	03/17/92		0.9	5.7	1.9	0.1	
Mill A	5b	03/17/92	D	1.2	4.6	1.9	0.2	
Mill B	2a	02/20/92		0.4	1.7	1.2	0.1	0.4
Mill B	2b	02/20/92	D	0.4	1.4	0.8		0.2
Mill B	4a	03/02/92		1.0	9.1	3.0		
Mill B	4b	03/02/92	D	0.9	8.7	2.3		
Mill B	5a	03/09/92		0.6	3.9	1.3		
Mill B	5b	03/09/92	D	0.5	3.0	1.5		
Mill B	6a	03/16/92		0.1	0.4	0.2	0.1	
Mill B	6b	03/16/92	D	0.1	0.5	0.2		
Mill B	7a	03/24/92		0.6	2.4	2.1		
Mill B	7b	03/24/92	D	0.6	2.6	2.3		
Mill C	2a	02/26/92		0.3	0.2	0.2		0.2
Mill C	2b	02/26/92	D	0.4	0.1	0.2	0.1	0.4
Mill C	4a	03/11/92						
Mill C	4b	03/11/92	D					
Mill C	5a	03/17/92			0.2	0.3	0.1	
Mill C	5b	03/17/92	D		0.4	0.3		
Mill C	7a	03/31/92		0.2	0.4	0.6		
Mill C	7b	03/31/92	D	0.3	0.4	0.8		

PPCP Duplicate Analysis Results

Source	Set	Date	Duplicate	35_DCC ug/L	45_DCC ug/L	345_T3CC ug/L	346_T3CC ug/L	T4CC ug/L
Mill A	2a	02/25/92		1.5	35.0	13.1	0.5	1.0
Mill A	2b	02/25/92	D	1.2	32.0	12.1	0.5	0.9
Mill A	4a	03/10/92		2.0	23.2	16.2	0.5	0.8
Mill A	4b	03/10/92	D	1.8	31.0	15.7	0.4	0.9
Mill A	5a	03/17/92		0.5	26.4	10.1	0.4	0.9
Mill A	5b	03/17/92	D	0.7	24.4	14.9	0.4	0.8
Mill B	2a	02/20/92		0.3	2.3	3.1		0.5
Mill B	2b	02/20/92	D	0.2	1.5	2.3		0.4
Mill B	4a	03/02/92		1.0	7.9	13.0		1.1
Mill B	4b	03/02/92	D	0.7	7.8	11.2	0.2	1.0
Mill B	5a	03/09/92		0.7	6.8	7.6	0.2	0.7
Mill B	5b	03/09/92	D	0.7	5.0	9.0		0.5
Mill B	6a	03/16/92		0.1	0.9	1.3		
Mill B	6b	03/16/92	D		1.3	1.2		
Mill B	7a	03/24/92		0.2	2.0	2.9		0.4
Mill B	7b	03/24/92	D		1.5	3.1		0.4
Mill C	2a	02/26/92		0.1	0.6	0.3		
Mill C	2b	02/26/92	D	0.1	0.5	0.4		
Mill C	4a	03/11/92			0.6			
Mill C	4b	03/11/92	D					
Mill C	5a	03/17/92		0.3	1.8	0.5		
Mill C	5b	03/17/92	D	0.5	1.8			
Mill C	7a	03/31/92			0.4			
Mill C	7b	03/31/92	D		0.4			

PPCP Duplicate Analysis Results

Source	Set	Date	Duplicate	45_DCV ug/L	345_T3CV ug/L	T4CV ug/L	456_T3CS ug/L
Mill A	2a	02/25/92		1.0	2.1	0.2	0.1
Mill A	2b	02/25/92	D	0.9	1.7	0.2	0.1
Mill A	4a	03/10/92		1.1	0.8		
Mill A	4b	03/10/92	D	1.5	0.5		
Mill A	5a	03/17/92		1.0	0.9		0.1
Mill A	5b	03/17/92	D	1.2	1.0		
Mill B	2a	02/20/92			0.4		
Mill B	2b	02/20/92	D		0.4		
Mill B	4a	03/02/92			0.7		
Mill B	4b	03/02/92	D		0.7		
Mill B	5a	03/09/92			0.9		
Mill B	5b	03/09/92	D		1.0		
Mill B	6a	03/16/92			0.4		
Mill B	6b	03/16/92	D		0.4		
Mill B	7a	03/24/92			0.6		
Mill B	7b	03/24/92	D		0.6		
Mill C	2a	02/26/92					0.3
Mill C	2b	02/26/92	D				0.4
Mill C	4a	03/11/92		0.3			
Mill C	4b	03/11/92	D				0.2
Mill C	5a	03/17/92		0.5			0.5
Mill C	5b	03/17/92	D	0.4			0.5
Mill C	7a	03/31/92					0.1
Mill C	7b	03/31/92	D		0.1		0.1

APPENDIX C

SUMMARY OF PPCP QA/QC SPIKING RESULTS

PPCP MDL SUMMARY

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	50 ug Spike Recovery				Duplicate Differences			
Compound	Average Percent Recovery	Average Recovery (ug)	Standard Deviation (ug)	n	Standard Deviation	n	Method Detection Limits Recovery (ug/L)	Duplicates (ug/L)
Guaiacols								
4_CG	114	0.0570	0.0058	11			0.017	
45_DCG	109	0.0517	0.0057	11	0.0030	12	0.017	0.009
46_DCG	100	0.0498	0.0029	11	0.0012	2	0.009	0.004
345_T3CG	114	0.0568	0.0191	11	0.0093	12	0.057	0.028
346_T3CG	102	0.0511	0.0054	11	0.0079	7	0.016	0.024
456_T3CG	109	0.0543	0.0102	11	0.0009	9	0.031	0.003
T4CG	104	0.0522	0.0107	11	0.0054	9	0.032	0.016
Catechols								
4_CC	98	0.0492	0.0048	11			0.015	
34_DCC	84	0.0421	0.0044	11			0.013	
35_DCC	92	0.0461	0.0036	11	0.0054	2	0.011	0.016
45_DCC	93	0.0466	0.0062	11	0.0030	10	0.019	0.009
345_T3CC	90	0.0448	0.0078	11	0.0057	11	0.023	0.017
346_T3CC	69	0.0344	0.0072	8			0.022	
T4CC	53	0.0263	0.0073	11			0.022	

APPENDIX D

AEC METHOD NO. AE130.0

CHLORINATED PHENOLIC COMPOUNDS IN BLEACHED KRAFT MILL EFFLUENTS AND RECEIVING WATERS

1. Scope and Application

1.1 This method describes the procedure for target compound analysis of bleached kraft pulp mill effluents (BKME) and receiving waters for chlorinated phenols, guaiacols, catechols and veratroles. The method involves *in situ* acetylation of phenolics groups during extraction into methyl-*t*-butyl ether followed by analysis by capillary gas chromatography coupled mass spectrometry (GC/MS) with a mass selective detector (MSD) operated in the selected ion monitoring (SIM) mode.

1.2 This method is directly applicable to samples containing phenols, guaiacols, catechols, and veratroles in concentrations between 0.05 to 100 µg/L. Samples with higher concentrations of chlorinated phenolics require dilution prior to analysis.

1.3 All the compounds determined with this method, along with their current method detection limits (MDL), are listed in Table 1.

2. Summary of Method

2.1 This method consists of two steps:

2.1.1 Extraction of the chlorinated phenolics into methyl-*t*-butyl ether, with *in situ* acetylation, using a within sample bottle extraction with magnetic stirring being used for agitation.

2.1.2 Analysis of the acetylated extract by GC/MSD in the SIM mode.

2.2 Surrogate standards are added to samples or diluted samples prior to extraction to assess extraction efficiency. An internal standard is added prior to instrumental analysis and is used for quantitation.

3. Interferences

3.1 Chlorinated phenolic compounds are susceptible to both oxidation, and hydrolysis of chloride. Procedures for preservation and storage must be strictly observed.

Table 1. Pulp and Paper Related Chlorinated Phenolic Compounds (PPCP); Method Performance in Fortified Reagent Water

Compound	Fortified Reagent Water[1]		
	Mean Recovery (%) (n=7)	Relative Standard Deviation (µg/L)	Method Detection Limit[2] (µg/L)
Chlorinated Phenols			
2-Chlorophenol	76.0	11.3	0.008
2,4-Dichlorophenol	67.7	21.0	0.013
2,4,6-Trichlorophenol	72.9	11.7	0.008
2,3,4,6-Tetrachlorophenol	48.3	31.5	0.014
Pentachlorophenol	46.1	27.4	0.012
Chlorinated Guaiacols			
4-Chloroguaiacol	105.7	9.3	0.009
4,5-Dichloroguaiacol	79.8	9.1	0.007
4,6-Dichloroguaiacol	72.9	11.6	0.008
3,4,5-Trichloroguaiacol	77.8	17.2	0.013
3,4,6-Trichloroguaiacol	67.8	27.4	0.016
4,5,6-Trichloroguaiacol	73.0	19.0	0.013
Tetrachloroguaiacol	74.5	11.6	0.008
Chlorinated Catechols			
4-Chlorocatechol	65.4	15.8	0.010
3,4-Dichlorocatechol	74.0	12.8	0.009
3,5-Dichlorocatechol	64.9	26.4	0.016
4,5-Dichlorocatechol	68.0	30.3	0.019
3,4,5-Trichlorocatechol	76.2	23.1	0.017
3,4,6-Trichlorocatechol	56.5	28.5	0.015
Tetrachlorocatechol	56.7	35.0	0.018
Other Chlorinated Phenolic Compounds			
4,5-Dichloroveratrole	77.0	15.8	0.011
3,4,5-Trichloroveratrole	78.0	15.2	0.011
Tetrachloroveratrole	64.9	32.9	0.020
4,5,6-Trichlorosyringol	79.5	20.4	0.015

[1] Samples (0.8 L) were fortified with 25 ng of each component.

[2] Based on three times the standard deviation from the analysis fortified 0.8 L sample. Confirmation ions may not be observed at these concentrations.

4. Sample Collection, Preservation and Handling

4.1 A 1 L amber glass bottle cleaned and verified by **SOP SB10.0** is filled directly with greater than 0.8 L of sample. Add to the sample ascorbic acid (0.4 g) and one vial of nitric acid preservative (see Section 6.1.3) which will acidify the sample to between pH 1.5 and 2.5.

4.2 Samples must be stored on ice immediately after sampling and then refrigerated a 4°C until the time of extraction.

4.3 All samples should be extracted within 14 days.

5. Safety

5.1 The laboratory maintains material safety data sheets (MSDS) for all chemicals involved in this method. This material is available to all personnel involved in the chemical analysis.

6. Apparatus and Materials

6.1 Sampling Equipment.

6.1.1 Sample bottle, 1 L, amber glass as described in **SOP SB10.0**.
6.1.2 Ascorbic acid, 99+% ACS reagent grade.
6.1.3 One vial of nitric acid preservative (5 mL of 1:1 HNO_3).

6.2 Labware - all glassware prepared using **SOP SA22.0.**

6.2.1 Gas tight syringes, 10 µL, 25 µL, 100 µL, 250 µL, 500 µL, and 1000 µL.
6.2.2 Separatory funnels, 1 L.
6.2.3 Magnetic stirring bar, 3/8" x 2".
6.2.4 Short stem glass funnel, 8 cm diameter.
6.2.5 Volumetric pipettes and bulb, 4 mL, 5 mL, 50 mL and 100 mL.
6.2.6 Pasteur pipettes, 5" and 9".
6.2.7 Glass screw capped vials (2 mL) with Teflon lined screw caps.
6.2.8 Distillation apparatus with distillation column.

6.2.9 Kuderna-Danish (K-D) concentration apparatus.

6.2.9.1 Concentrator tube, 10 mL, graduated.

6.2.9.2 Evaporation flask, 500 mL.

6.2.9.3 Snyder column, 3 ball macro.

6.2.9.4 Snyder column, micro.

6.2.10 Filter paper, 12.5 cm, Whatman No. 1 or equivalent.

6.2.11 Graduated cylinders, 50 mL, 100 mL and 1 L.

6.2.12 Teflon boiling chips.

6.3 Equipment

6.3.1 Water bath capable of heating the K-D apparatus to 70°C.

6.3.2 Magnetic stirrer.

6.3.3 pH Meter capable of reading ± 0.05 pH units.

6.3.4 Analytical balance capable of reading ± 0.0001 g.

6.3.5 Metered source of nitrogen gas, 5 psig, high purity.

7. Chemicals and Reagents

7.1 Ascorbic acid, 99+% ACS reagent grade.

7.2 Acetic anhydride, reagent grade, freshly distilled.

7.3 Methyl-*t*-butyl ether, 2,2,4-trimethylpentane, pesticide grade, or equivalent.

7.4 Reagent water, ASTM grade II or better.

7.5 Potassium carbonate (75% in water), analytical reagent grade.

7.6 Sodium hydroxide (10% in reagent water), analytical reagent grade.

7.7 Sodium hydroxide (40% in reagent water), analytical reagent grade.

7.8 Anhydrous sodium sulphate, analytical reagent grade, prepared using **SB03.0**.

7.9 Standard solutions prepared using **SOP SB17.0**:

7.9.1 Internal standard spiking solution.

7.9.2 Surrogate standard spiking solution.

7.9.3 Composite standard solution, 50 µg/mL of each component.

7.9.4 Instrument calibration standard solutions.

8. Sample Extraction

8.1 Shake vigorously samples of receiving waters, in their containers (1 L amber glass bottles), to resuspend any particulate material present. Pour off approximately 200 mL of the sample to leave approximately 800 mL of sample in the bottle. Mark the level of sample so that the volume of sample may be determined later.

8.2 Dilute effluent samples prior to analysis. Transfer to pipette, aliquots of resuspended effluent samples to 1 L amber glass bottles and dilute to 800 mL with reagent water. Typically, aliquots of 100 mL of biologically treated and 50 mL of untreated bleached kraft mill effluent are extracted.

8.3 Add approximately 0.4 g of ascorbic acid and a magnetic stirring bar to the sample. Adjust the sample pH to between pH 7.5 and 8.5 using first aliquots of 40% sodium hydroxide solution until the pH just exceeds 3, followed by aliquots of 10% sodium hydroxide solution. Spike the sample with 10 µL of the surrogate standard spiking solution.

8.4 Add 10 mL of the 75% potassium carbonate solution and 4 mL of freshly distilled acetic anhydride, while the sample is gently stirred.

8.5 Once these acetylation reagents have been added, extract the samples immediately using a stir bar method as described in **SOP SA06.0**.

8.6 Concentrate the acetylated sample extracts using a Kuderna-Danish apparatus as described in **SOP SA14.0**, exchanging the solvent to 2,2,4-trimethylpentane and concentrating to approximately 1 mL.

8.7 Spike the concentrated extracts with 5 µL of internal standard spiking solution, transfer to a 2 mL glass screw cap vial fitted with a Teflon lined screw cap or septum, and store at -20°C until analyzed.

8.8 Determine the volume of the sample extracted by filling the empty sample bottle to the mark made prior to extraction (Section 8.1) with water, then decant the water into a 1 L graduated cylinder. Read the volume to the nearest 5 mL and record the results.

Table 2. Ions and Retention Times of Chlorinated Phenolic Acetates

Compound	Retention Time (min)	Quantification Ion (m/e)	Confirmation Ions (m/e)	(m/e)
Chlorinated Phenols				
4-Chlorophenol	10.13	128	130	170
2,4-Dichlorophenol	12.46	162	164	206
2,4,6-Trichlorophenol	14.75	196	198	238
2,3,4,6-Tetrachlorophenol	19.56	232	230	178
Pentachlorophenol	24.39	266	264	308
Chlorinated Guaiacols				
4-Chloroguaiacol	14.04	158	160	143
4,5-Dichloroguaiacol	18.51	192	194	177
4,6-Dichloroguaiacol	17.10	192	194	177
3,4,5-Trichloroguaiacol	21.68	226	228	211
3,4,6-Trichloroguaiacol	19.99	226	228	211
4,5,6-Trichloroguaiacol	22.41	226	228	211
Tetrachloroguaiacol	25.04	262	260	264
Chlorinated Catechols				
4-Chlorocatechol	16.70	144	146	186
3,4-Dichlorocatechol	20.32	178	180	220
3,5-Dichlorocatechol	19.29	178	180	220
4,5-Dichlorocatechol	21.03	178	180	220
3,4,5-Trichlorocatechol	24.35	212	214	254
3,4,6-Trichlorocatechol	22.63	212	214	254
Tetrachlorocatechol	27.40	248	246	250
Other Chlorinated Phenolic Compounds				
4,5-Dichloroveratrole	16.22	206	208	191
3,4,5-Trichloroveratrole	19.67	240	242	225
Tetrachloroveratrole	21.68	261	259	276
4,5,6-Trichlorosyringol	25.42	256	258	241

9. Cleanup and Separation

9.1 Cleanup and separation methodology is under development.

10. Gas Chromatography/Mass Spectrometry

10.1 A Hewlett Packard 5970 MSD coupled to a Hewlett Packard 5890 GC equipped with an split/splitless capillary injector and a Hewlett Packard 7673A automated liquid sampler is used for this analysis. Other GC/MS systems capable of selected ion monitoring and split/splitless capillary injection may be used.

10.2 Gas chromatography is performed with a 25 m 0.20 mm I.D. Ultra-1 (bonded methylsilane) column with a split/splitless capillary injector run in the splitless mode at 250°C. The injector purge is turned on 1.0 min after injection. Helium (20 psig, ca 30 cm/sec at 175•C) is used as the carrier gas. The initial oven temperature is 50°C, held for 2 min then increased at a rate of 15°C/min to 125°C and then increased at a rate of 4°C/min to 250°C.

10.3 Selected ion mass spectrometry is performed with the MSD using autotune parameters but with the electron multiplier 400 eV greater than the autotune value and with the low mass resolution option selected. Table 2 gives the ions and retention times of the target analytes using the above GC/MSD conditions.

11. Calibration

11.1 An internal standard method using log/log relative response curves of up to eight levels of calibration to generate calibration curves is used.

11.2 Calibration standard solutions, the internal standard spiking solution, the 50 µg/mL composite standard spiking solution and the surrogate standard spiking solutions are prepared using **SOP SB17.0**. The volumes of aliquots of the spiking solutions used to prepare 10 mL calibration standard solutions are listed in Table 3.

11.3 Calibration solutions are analyzed with samples during routine analysis.

11.4 Calibration curves of relative response versus amount are compiled for each analyte after analysis and calibration equations are calculated using log/log linear regression.

Table 3. Aliquots of Pulp and Paper Chlorinated Phenolic Compounds (PPCP) Standard Solutions Used to Prepare Instrument Calibration Standard Solutions

Standard Number	PPCP Mixed Standard Solution (µL)	Internal Standard Spiking Solution (µL)	Surrogate Standard Spiking Solution (µL)
PPCP-1	1000	50	100
PPCP-2	500	50	100
PPCP-3	200	50	90
PPCP-4	100	50	80
PPCP-5	50	50	70
PPCP-6	20	50	60
PPCP-7	10	50	50
PPCP-8	5	50	40

12. Calculations

12.1 The relative response of a component is calculated by dividing the peak height of the component ($Resp_{Comp}$) by the peak height of the internal standard ($Resp_{IS}$). The relative response factor is the relative response divided by the amount of compound analyzed (Amt_{Comp}). The concentration of the internal standard can be neglected in this calculation as it is constant for all analysis with this method.

12.2 Estimates of the slope (A) and exponential (B) terms for log/log response equations (of the form of Equation 1) for all analytes are calculated using log/log least squares fits of results of the analysis of calibration solutions.

$$Log\frac{Resp_{Comp}}{Resp_{IS}} = A + B \times Log(Amt_{Comp}) \qquad (1)$$

12.3 Concentrations of analytes in samples are calculated by substitution in equation 1.

13. Reporting of data

13.1 All non-negative data generated using this method are reported. Each report of analysis must also contain the method detection limits for each analyte. Results in which a confirmation ion is not observed, or is observed in the wrong ratio (Section 14.3) are reported in parentheses. It is left to the client to best judge how to use the data below detection limits or tentatively confirmed, although the analyst should render any assistance

or advise possible.

13.2 When data are adjusted for recovery, the average of the recoveries of 2,3,6-trichlorophenol and 2,6-dibromophenol is used (for the recovery factor). This recovery factor is applied to all analytes.

13.3 Results in which the most significant figure (first digit) is a 1 or 2, are reported to three significant figures. All other results are reported to two significant figures.

14. Quality Assurance/Quality Control

14.1 QA/QC of extraction

14.1.1 Analysis of blanks. At least one full method blank is analyzed with every ten samples.

14.1.2 Analysis of duplicates. A minimum of one set of duplicate analysis is performed with every ten samples. The results of these analyses are used to estimate the precision of the method.

14.1.3 Analysis of fortified samples. A duplicate sample, fortified with the 100 µg/mL composite standard solution at a level comparable to the concentrations of analytes expected is analyzed with every twenty samples. The results of these analyses are used to estimated the recovery of analytes.

14.1.4 Analysis of surrogate standards. All samples are spiked with surrogate standards and their recoveries are calculated.

14.2 QA/QC of instrumental analysis

14.2.1 The mean and standard deviation of within batch internal standard responses are plotted on control charts.

14.2.2 Calibration parameters of all analytes are plotted on control charts.

14.2.3 The calibration curves must be linear and approximately first order with the exponential term not less than 0.9 and not greater than 1.1.

14.2.4 Quantitation ions of analytes must elute within 0.05 minutes of the calibration retention time and coelute with the two confirmation ions. Results where both confirmation ions are not present are flagged.

14.3 QA/QC of GC/MSD peak identification.

14.3.1 Analytes are initially recognized using ion chromatograms of quantification ions. The ratio of an analyte's relative retention time in the sample, to that of a standard, must not deviate from 1 by more than 0.005. This tolerance may be revised at a later date when more operational data are available.

14.3.2 The identity of an observed analyte (Section 14.3.1) is confirmed using ion chromatograms of the analyte confirmation ions. The retention time of the confirmation ions must deviate from that of the quantification ion by more that 0.015 min. The ratio of the response of the confirmation ion(s) must not deviate significantly (± 30%) from those observed in the analysis of standards. Specific tolerances may be included in later revisions of this method.

14.3.3 If only one confirmation ion, meeting the above criteria, is observed, the result is reported, but with a flag. If no confirmation ion is observed, the analyte is not considered to be detected. However, in the case of analysis of blanks, all results are included in any background subtraction calculations.

14.4 Additional QA/QC procedures are under development.

15. Method Performance

15.1 The method detection limit (MDL) is defined as the minimum detected concentration of a substance that can be measured with 99% confidence that the true value is above zero. This concentration is three times the method noise or standard deviation. The method standard deviation is estimated from the calculated standard deviation of seven or more low level (5 to 10 x MDL) reagent water spikes, and only applies to "clean" matrices. MDLS were obtained when instrumentation was optimized. During routine analyses, instrumental detection limits may exceed the MDL.

15.2 Method detection limits and recoveries for analytes are listed in Table 1.

16. References

16.1 B. Starck, P.E. Bethge, M. Gergou and E. Talka. Determination of Chlorinated Phenols in Pulp Mill Effluents, **Paperi Puu. 67**(12), 745 (1985).

16.2 H-B Lee, R.L. Hong-You, and P.J.A. Fowlie. Chemical Derivatization Analysis of Phenols. Part VI. Determination of Chlorinated Phenolics in Pulp and Paper Effluents, **J. Assoc. Off. Anal. Chem. 72**(6), 979 (1989).

16.3 R.H. Voss, J.T. Wearing and A. Wong. A Novel Gas Chromatographic Method for the Analysis of Chlorinated Phenolics in Pulp and Paper Effluents in Advances in the Identification and Analysis of Organic Pollutants in Water, L.H. Keith ed., Volume 2. Ann Arbor Science Publ. Inc., Ann Arbor, 1059-1095 (1985).

RMMAE130.S1F

STIR BAR EXTRACTION

1. Introduction

1.1 This standard operating procedure (SOP) describes the procedure for extraction using magnetic stirring for agitation. It is specific to extraction with solvents which are lighter than water.

1.2 This procedure is applicable to extraction of surface waters and diluted effluents.

1.3 The solvent used in this standard operating procedure is methyl-*t*-butyl ether.

2. Apparatus and Materials

2.1 Labware. Glassware is prepared using the appropriate SOP.
- 2.1.1 Separatory funnels, 1 L.
- 2.1.2 Short stem glass funnels, 8 cm diameter.
- 2.1.3 Graduated cylinders, 1 L, 100 mL, 50 mL.
- 2.1.4 Magnetic stir bars, 3/8 x 2".
- 2.1.5 Glass bottles, 1 L, amber, with Teflon lined screw caps.
- 2.1.6 Filter paper, 12.5 cm, Whatman No. 1 or equivalent.

2.2 Equipment.
- 2.2.1 Magnetic stirrer.
- 2.2.2 Retort stand, rings and clamps.

2.3 Chemicals and Reagents.
- 2.3.1 Methyl-*t*-butyl ether, pesticide grade or equivalent.
- 2.3.2 Anhydrous sodium sulphate, ACS reagent grade.
- 2.3.3 Sodium chloride, ACS reagent grade.
- 2.3.4 Reagent water, ASTM grade II or better.

3. Sample Extraction

3.1 Shake vigourously the surface water samples, in 1 L amber glass bottles to resuspend any particulate material present. Pour off approximately 200 mL of the sample to

leave approximately 800 mL of sample in the bottle. Mark the level of sample in the bottle so that the volume of sample may be determined later.

3.2 If effluent samples are to be extracted and require dilution (as specified in an analytical method), transfer by pipette, aliquots of the sample to a 1 L amber glass bottle and dilute to 800 mL with reagent water.

3.3 Adjust the pH of the sample if required and add surrogate standards, as directed in the analytical method in use. Derivatization procedures, if applicable, are then performed as described in the analytical method.

3.4 Add the extraction solvent (100 mL of methyl-*t*-butyl ether) to the sample and stir the system by magnetic stirring for 1 h. The vortex should descend at least a third of the way down the bottle.

3.5 Transfer the sample to a 1 L separatory funnel and allow the phases to separate. Collect the aqueous phase in the sample bottle. Filter the organic fraction through a solvent rinsed filtering system of 6 g of anhydrous sodium sulphate, held in a 12.5 cm Whatman No. 1 filter (fluted) and a short stem glass funnel. Collect the extract in the concentration vessel as specified in the analytical method.

3.6 Repeat twice the extraction procedure as described in Section 3.4 and 3.5 with 50 mL of methyl-*t*-butyl ether. Dry the combined extracts and collect in the concentration vessel.

3.7 Rinse the separatory funnel with 50 mL of methyl-*t*-butyl ether. Use this rinse to wash the sodium sulphate filter cake.

3.8 Although this filtering method uses less agitation than a hand extraction with a separatory funnel, emulsions are sometimes formed. If higher detection limits are acceptable, emulsions may be avoided by diluting the sample and rerunning the extraction. If this is not acceptable, then the emulsion must be "broken" prior to filtration through sodium sulphate.

3.8.1 To remove the emulsion, allow the sample to stand in the separatory funnel the maximum possible time. Remove as much of the aqueous layer as possible and after over 750 mL is removed, proceed with the subsequent extraction.

3.8.2 If the emulsion still remains in the organic layer after the subsequent extraction, then transfer the sample to the same separatory funnel and pool the organic layers in the separatory funnel.

3.8.3 If the emulsion remains after allowing the emulsion to stand 0.5 h after the completion of the three extractions, attempts to "break" the emulsion may be made by either centrifugation or adding 50 mL of saturated aqueous sodium chloride and gently swirling the mixture.

3.8.4 If the emulsion comprises no more than 10% of the extract volume, filter the extract through anhydrous sodium sulphate. The filter cake must be constantly monitored for saturation with water, and additional sodium sulphate must be added as required, during the filtration. After the extract has been filtered, wash the separatory funnel and the filter cake twice with 50 mL aliquots of methyl-*t*-butyl ether.

3.8.5 The methods used to handle the emulsions as well as the effected samples must be noted in the analyst's laboratory note book.

4. Safety

4.1 Methyl-*t*-butyl ether is flammable and inhalation of its vapours may cause drowsiness, headaches or nausea. Operations which allow the release of these vapours in the air, such as filtration, must be performed in a fumehood.

CONCENTRATION OF EXTRACTS WITH KUDERNA-DANISH CONCENTRATORS

1. Introduction

1.1 This standard operating procedure describes the concentration of solvent extracts with Kuderna-Danish concentrators. This method of concentration is more cumbersome and laborious than those using rotary evaporators, but affords higher and reproducible recoveries of semivolatile organic compounds such as naphthalene and phenols.

1.2 Care must be taken with oxidatively labile compounds, as the concentration takes place in an open atmosphere.

1.3 This standard operating procedure is designed specifically to concentrate methyl-*t*-butyl ether extracts, but may be used to concentrate other solvents with similar boiling points.

2. Apparatus and Materials

2.1 Glassware prepared using **SOP SA22.0.**

2.1.1 Concentrator tube, 10 mL, graduated.

2.1.2 Kuderna-Danish (K-D) evaporation flask, 500 mL.

2.1.3 Snyder column, 3 ball macro.

2.1.4 Snyder column, micro, 3 stage.

2.1.5 Teflon boiling chips.

2.2 Equipment.

2.2.1 Water bath capable of heating K-D apparatus to 70°C.

2.2.2 Retort stand and clamps.

2.3 Chemicals and Reagents[1].

2.3.1 Methyl-*t*-butyl ether and 2,2,4-trimethylpentane, pesticide grade or equivalent.

[1] Substitutes for the solvents listed below may be specified in the analytical methods.

3. Procedure

3.1 For each sample, transfer the combined dried extracts and rinses to a 500 mL K-D evaporation flask fitted with a graduated 10 mL concentration tube.

3.2 Add two Teflon boiling chips to the K-D apparatus before fitting the macro Snyder column. Hold the K-D apparatus in a 60-70°C water bath and swirl gently until the solvent starts to boil.[2] Clamp the apparatus in the water bath and let the solvent evaporate at reflux. The rate of reflux must not be high enough to flood chambers in the Snyder column. The rate of reflux can be controlled by either adjusting the temperature of the water bath or raising or lowering the K-D apparatus in the water bath.

3.3 Concentrate the sample to approximately 10 mL. Rinse the apparatus with 25 mL of methyl-*t*-butyl ether and then concentrate to approximately 4 mL.

3.4 Cool the K-D apparatus and then detach the Snyder column. Rinse the inside surface of the evaporation flask into the concentrator tube with approximately 2 mL of methyl-*t*-butyl ether.

3.5 Detach the evaporation flask and fit the concentrator tube with a micro Snyder column. Add another Teflon boiling chip and place apparatus in water bath, swirling gently until the solvent starts to boil. Concentrate to approximately 2 mL and add 1 mL 2,2,4-trimethylpentane.

3.6 Remove apparatus from the bath and allow to cool. Concentrate the extract to 1 mL (or the volume specified in the method) under a stream of nitrogen.

4. Safety

4.1 Methyl-*t*-butyl ether is flammable and inhalation of its vapours may cause drowsiness, headaches or nausea. All concentration operations must be performed in a fumehood.

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[2] It is important not to superheat the sample, as superheated solvent may begin to boil rapidly and be blown out of the Snyder column.

PREPARATION OF GLASSWARE FOR THE ANALYSIS OF PULP AND PAPER RELATED SAMPLES

1. Introduction

1.1 This standard operating procedure describes the preparation of glassware used for the analysis of pulp and paper related samples for adsorbable organic halide, resin and fatty acids, or pulp and paper related chlorophenolic compounds.

1.2 This procedure excludes the use of a laboratory dish washer. The glassware is washed by hand in an area free of chlorinated solvents. Very thorough rinsing is involved to ensure that no traces of detergent remain on the glassware. No oxidants, such as chromic acid, may be used in this procedure. Glassware prepared using this procedure is not oven dried, and kept separate from other glassware.

2. Apparatus and Materials

2.1 Labware

2.1.1 Sparkleen glassware detergent.

2.1.2 Plastic basin, 10 L capacity.

2.1.3 Test tube brushes, sizes depending on glassware.

2.2 Equipment

2.2.1 Ultrasonic bath, 20 L capacity.

2.2.2 Source of hot water.

2.2.3 Reagent water, ASTM grade II or better.

3. Glassware Washing Procedure

3.1 Soak the glassware in a plastic basin filled with hot detergent solution, prepared as directed on the detergent package (5 mL of detergent in 1 L of water). The time spent soaking will depend on the initial state of the glassware but must not exceed 4 hours. Loosen all Teflon fittings, such as stopcocks, to expose the glass surfaces to the detergent, and to prevent the expansion of the Teflon fittings which could crack the glass housings. The fittings are not completely removed from the associated glassware unless necessary and if removed, are replaced as soon as possible. These fittings are not treated as interchangeable.

3.2 After soaking, scrupulously scrub all surfaces of the glassware with the appropriately sized brush. Inspect brushes prior to use to ensure that the bristles are in good condition and use of the brush will not cause scratching of the glassware. If any deposits on the glassware cannot be dislodged by scrubbing the glassware is set aside for washing in the ultrasonic bath.

3.3 After scrubbing, rinse thoroughly all surfaces of the glassware with hot water. This rinsing process is repeated five times. After rinsing with hot water, thoroughly rinse all surfaces of the glassware with reagent water. This process is repeated five times.

3.4 After rinsing, inspect the glassware for any evidence of deposits or soap films. Deposits and films may be obvious to the eye or may be detected by the way the water coats the glassware. On clean glassware the water will bead and not form a thin film. Any glassware requiring further cleaning is set aside for washin in the ultrasonic bath.

3.5 After inspection, store the glassware. It must, however, be inspected again and solvent rinsed (except in the case of AOX analysis) immediately prior to use.

4. Glassware Washing Procedure with the Ultrasonic Bath

4.1 Place the glassware in an ultrasonic bath filled with hot detergent solution, prepared as directed on the detergent package (5 mL of detergent in 1 L of water). Loosen all Teflon fittings, such as stopcocks, to expose the glass surfaces to the detergent and to prevent the expansion of the Teflon fittings. Turn on the ultrasonic bath for 0.5 hour.

4.2 Follow rinsing and inspection procedures described in Sections 3.2 to 3.5.

PREPARATION OF SODIUM SULPHATE

1. Introduction

1.1 The purpose of this standard operating procedure is to specify the methods for cleaning, preparing, and storing sodium sulphate.

1.2 Sodium sulphate is used to remove residual traces of water from organic solvent extracts. Acidified sodium sulphate is used to ensure the best recovery possible for certain organics and pesticides with acidic functional groups.

2. Apparatus and Materials

2.1 Glassware.
- 2.1.1 Four litre beaker.
- 2.1.2 Two litre filtering flask.

2.2 One litre Buchner funnel.

2.3 Whatman paper, #4.

2.4 Muffle furnace.

2.5 Two litre crucible.

3. Reagents

3.1 Sodium sulphate, ACS granular, anhydrous.

3.2 Methylene chloride and diethyl ether, pesticide quality or equivalent.

3.3 Concentrated sulphuric acid (36N), analytical reagent grade.

4. Preparation and Storage

4.1 Sodium sulphate. Add the contents of a five pound jar (2.3 kg) to a 2 L crucible and heat in a muffle furnace to 400°C for a minimum of 4 h. After cooling, store the material in a precleaned (solvent rinsed, then dried) amber glass jar with a Teflon-lined cap.

4.2 Acidified sodium sulphate. To a slurry of 2.3 kg of sodium sulphate in 1 L of methylene chloride in a 4 L beaker add a solution of 5 mL of 36N sulphuric acid and 125 mL of diethyl ether and stir for 5 min. Filter the sodium sulphate using a 1 L Buchner funnel with #4 Whatman filter paper under vacuum, and dry under vacuum for 10 min. Store the material in a precleaned (see Section 4.1) amber glass jar with a Teflon lined cap.

PREPARATION OF CALIBRATION STANDARDS FOR PULP AND PAPER CHLORINATED PHENOLIC COMPOUNDS

1. Introduction

1.1 This standard operating procedure describes the procedure used to prepare acetylated calibration standards for the analysis of pulp and paper related chlorophenolic compounds. These standards are acetylated in a solution of acetic anhydride, toluene and pyridine to achieve a high yield of the acetates, with a low variation in yield, between preparations.

1.2 These standards are not prepared with individually prepared phenolic acetates, because with the high number of analytes (22) this is not practical, and in the case of some analytes, preparation of the pure acetates would be prohibitively expensive.

2. Summary of the Procedure

2.1 Individual primary standard solutions of all analytes (Table 1), surrogate standards and the internal standard are prepared. From these a 50 µg/mL mixed standard solution is prepared by combining aliquots of the analyte primary standard solutions. Internal and surrogate spiking standard solutions are prepared by diluting the primary internal and surrogate standard solutions.

2.2 Calibration standard solutions are prepared by: 1. acetylation of aliquots of the mixed standard solution, the surrogate standard spiking solution and the internal standard spiking solution and; 2. dissolution of the acetylated standards in 2,2,4-trimethylpentane.

3. Apparatus and Materials

3.1 Labware, glassware prepared using **SOP SA22.0.**

3.1.1 Volumetric flasks, 10.00 mL and 25.00 mL.

3.1.2 Kuderna-Danish (K-D) concentrator tubes, 10 mL graduated.

3.1.3 Snyder condenser, micro, 3 stage.

3.1.4 Mixxor® extractor, 20 mL.

3.1.5 Syringes, 10, 50, 100, 500, 1000 and 5000 µL.

3.1.6 Pasteur pipettes, 5".

3.1.7 Glass screw cap tube, 15 x 200 mm, with Teflon lined screw caps.

3.1.8 Teflon boiling chips.

3.2 Equipment

3.2.1 Water bath capable of heating to 70° C.

3.2.2 Metered source of nitrogen, ultra high purity (UHP).

3.2.3 Retort stand and clamps.

3.2.4 Analytical balance, accurate to ± 0.0001 g, see **SOP SC02.0**.

3.3 Chemicals and Reagents

3.3.1 Standards of analytes, surrogates and internal standard listed in Table 1.

3.3.2 Toluene, 2,2,4-trimethylpentane, and methanol, pesticide grade.

3.3.3 Acetic anhydride, freshly distilled, ACS reagent grade.

3.3.4 Pyridine, ACS reagent grade.

3.3.5 Ascorbic acid, 99+% ACS reagent grade.

3.3.6 Anhydrous sodium sulphate, ACS reagent grade.

3.3.7 Reagent water, distilled deionized water.

4. Preparation of Spiking and Composite Standard Solutions

4.1 Prepare the primary standard solutions of all analytes and surrogates, (2-3 mg/mL concentrations) by dissolving accurately weighed amounts of reference standard material (20 to 30 mg, ± 0.1 mg) in 10.00 mL of nitrogen purged methanol (1 L purged at room temperature with a nitrogen flow rate of approximately 60 mL/min for 15 min) using a 10.00 mL volumetric flask. Prepare a primary standard solution of the internal standard, of approximately 5 µg/mL, is prepared by dissolving an accurately weighed amount (50 to 60 mg, ± 0.1 mg) in 10.00 mL of 2,2,4-trimethylpentane using a 10.00 mL volumetric flask. Transfer the primary standard solutions to a 15 x 200 mm screw cap glass tube, capp with a Teflon lined screw cap, and store at -20° C. These standard solutions are valid for 6 months.

4.2 Prepare a 50 µg/mL composite standard solution comprising all analytes by transferring, via syringe, aliquots of each primary standard solution, of the appropriate volumes (calculated to contain 1.25 mg of analyte), to a 25.00 mL volumetric flask. After the transfer of aliquots of all analytes is complete, dilute the combined aliquots to 25.00 mL with nitrogen purged methanol. Transfer the composite standard solution is transferred to three 15 x 200 mm screw cap glass tubes, cap with a Teflon lined

screw cap, and store at -20° C. This mixed standard solution is valid for 6 months.

Table 1. Chlorinated Phenolic Compounds Contained in Calibration Standards

Chlorinated Phenols	Chlorinated Guaiacols	Chlorinated Catechols	Misc. Chlorinated Compounds
2-Chlorophenol	4,5-Dichloroguaiacol	3,4-Dichlorocatechol	4,5-Dichloroveratrole
2,4-Dichlorophenol	4,6-Dichloroguaiacol	3,5-Dichlorocatechol	3,4,5-Dichloroveratrole
2,4,6-Trichlorophenol	3,4,5-Trichloroguaiacol	4,5-Dichlorocatechol	Tetrachloroveratrole
2,3,4,6-Tetrachlorophenol	3,4,6-Trichloroguaiacol	3,4,5-Trichlorocatechol	Trichlorosyringol
Pentachlorophenol	4,5,6-Trichloroguaiacol	3,4,6-Trichlorocatechol	
	Tetrachloroguaiacol	4-Chlorocatechol	
	4-Cloroguaiacol		
Internal Standard:	2,3,4,5-Tetrachlorobiphenyl		
Surrogate Standards:	2,3,6-Trichlorophenol; 2,6-Dibromophenol		

4.3 Prepare a spiking solution of the internal standard by diluting an aliquot of the primary standard solution, containing approximately 5 mg, to 25.00 mL with 2,2,4-trimethylpentane in a 25.00 mL volumetric flask. Transfer the solution to three 15 x 200 mm screw cap glass tubes, cap with a Teflon lined screw cap, and store at -20° C. This standard spiking solution is valid for 6 months.

4.4 Prepare a spiking solution of the surrogate standards by diluting aliquots of the primary standard solutions, containing approximately 2.5 mg of each surrogate standard, to 25.00 mL in nitrogen purged methanol in a 25.00 mL volumetric flask. Transfer the solution to three 15 x 200 mm glass screw cap tubes, cap with a Teflon lined screw cap, and store at -20° C. This standard spiking solution is valid for 6 months.

5. Preparation of Calibration Standards (includes acetylation)

5.1 Add the following to a graduated 10 mL K-D concentrator tube: approximately 10 mg of ascorbic acid; 0.1 mL of toluene; and, via syringe, the appropriate aliquots (volumes of aliquots listed in Table 2) of the 50 µg/mL composite standard solution and surrogate standard spiking solution for the calibration standard being prepared.

5.2 Fit a micro Snyder condenser to the tube and immerse the tube in the water bath (65-70°C) until the solvent is concentrated to 0.1 mL (may be very fast). Immediately, add 0.5 mL of acetic anhydride and 0.05 mL of pyridine to the tube and return it to the water bath for 1 hour. Remove the tube from the water bath and allow it to cool before adding 50 µL of the internal standard spiking solution. Transfer the contents of the tube, and two 5 mL reagent water rinses of the tube to the bottom of a 20 mL Mixxor® extractor.

5.3 Rinse the concentrator tube with 4 mL 2,2,4-trimethylpentane, and transfer to the Mixxor® extractor. This extractor is similar to a small separatory funnel, and extraction procedures oulined in **SOP SA05.0** are followed. Extract the original contents of the tube and the reagent water rinses. Elute the 2,2,4-trimethylpentane extract through a prerinsed, 1 g bed of anhydrous sodium sulphate contained in a 5" Pasteur pipette loosely plugged with glass wool. Collect the eluent in a 10.00 mL volumetric flask.

5.4 Repeat the procedure in Section 5.3 with 4 mL and then 2 mL of 2,2,4-trimethylpentane, and pool all the dried extracts in the 10.00 mL volumetric flask. Dilute the contents of the volumetric flask to 10.00 mL with 2,2,4-trimethylpentane. After thorough mixing, transfer the contents to a 15 x 200 mm Teflon lined screw cap glass tube and store capped at -20°C until required for calibration. This standard is valid for 6 months.

Table 2. Aliquots of Mixed and Spiking Standards for Preparing Calibration Standards

Standard Name	Mixed Standard (µL)	Surrogate Standard (µL)	Internal Standard (µL)
PPCP-1	5.0	50	50
PPCP-2	10.0	50	50
PPCP-3	20.0	75	50
PPCP-4	50	75	50
PPCP-5	100	75	50
PPCP-6	200	100	50
PPCP-7	500	100	50
PPCP-8	1000	100	50

6. Safety

6.1 Acetic anhydride, toluene and pyridine are volatile hazardous solvents. These chemicals should only be used in a fume hood. Prior to the use of these chemicals their material safety data sheets (MSDS) should be reviewed .

6.2 Chlorinated phenolic compounds all exhibit some acute toxicity and some have demonstrated chronic effects. Exposure of skin to these compounds should be avoided. Prior to the handling of these chemical their MSDS sheets should be reviewed.

APPENDIX E

SAS CODE USED TO EVALUATE SPLIT SAMPLE RESULTS

```
let varname=DCP24;      /* Set name of compound to be evaluated */
libname s  'D:\ian2';

title " Split Sample Analysis: &varname" ;

/*  This section Reads data from data file and logs the results of compound being evaluated
placing the results in data set tt */

data tt;
  set S.MODDUPAN ;
  logval = log10( &varname );
  format date date7.;
run;

/* This section calculates the difference of the log results and saves data in data set ttt */

proc sort data=tt; by mill set lab ; run;
data ttt;
  set tt;
  retain loga logb;

  by mill set ;
  if first.set then do;
    loga = . ; logb = . ;
  end;
  if lab eq 'A' then loga = logval ;
  if lab eq 'B' then logb = logval
 ;

  if last.set then do;
   logy = loga - logb ;
   output;
  end;
run;

/* Evaluated log ratio model using proc GLM and data set ttt */

PROC GLM DATA =TTT;
 CLASS MILL ;
 MODEL LOGY = MILL ;
 MEANS MILL / LSD SNK ;
 LSMEANS MILL / STDERR PDIFF;
RUN;

/* test for interactions between parameters and differences between Mill results using data set tt
*/

PROC GLM DATA =TT;
 CLASS MILL SET LAB date;
 MODEL LOGval = MILL date(MILL) LAB LAB*MILL;
 TEST H=MILL E=date(MILL) /ETYPE=3;
 MEANS MILL  LAB MILL*LAB / SNK ;
 LSMEANS MILL LAB MILL*LAB / STDERR PDIFF;
RUN;
```

APPENDIX F

SAS REPORTS OF EVALUATION OF SPLIT SAMPLE RESULTS

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: DCP24
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 14 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.00485065	0.00242532	0.13	0.8825
Error	11	0.21107006	0.01918819		
Corrected Total	13	0.21592071			

R-Square	C.V.	Root MSE	LOGY Mean
0.022465	-33.00595	0.13852	-0.41969

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.00485065	0.00242532	0.13	0.8825

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.00485065	0.00242532	0.13	0.8825

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 11 MSE= 0.019188
Critical Value of T= 2.20
Least Significant Difference= 0.2083
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 4.285714

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	-0.39023	3	PP
A	-0.41692	6	PG
A	-0.44067	5	WW

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 11 MSE= 0.019188
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 4.285714

Number of Means	2	3
Critical Range	0.2082739	0.2555723

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.39023	3	PP
A	-0.41692	6	PG
A	-0.44067	5	WW

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.41692431	0.05655114	0.0001	1
PP	-0.39023208	0.07997539	0.0005	2
WW	-0.44067307	0.06194867	0.0001	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.7903	0.7823
2	0.7903	.	0.6279
3	0.7823	0.6279	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 33 observations can be used in this analysis.

PPCP Split Samples - SAS Analysis Results

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	25	4.09610679	0.16384427	19.37	0.0002
Error	7	0.05921626	0.00845947		
Corrected Total	32	4.15532305			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.985749	4564.356	0.09198	0.00202

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	1.30306426	0.65153213	77.02	0.0001
DATE(MILL)	20	1.76375693	0.08818785	10.42	0.0020
LAB	1	1.02714339	1.02714339	121.42	0.0001
MILL*LAB	2	0.00214221	0.00107110	0.13	0.8830

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	1.63594579	0.81797289	96.69	0.0001
DATE(MILL)	20	1.97478084	0.09873904	11.67	0.0014
LAB	1	0.92226613	0.92226613	109.02	0.0001
MILL*LAB	2	0.00214221	0.00107110	0.13	0.8830

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	1.63594579	0.81797289	8.28	0.0024

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 7 MSE= 0.008459
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 10.8

Number of Means	2	3
Critical Range	0.0935814	0.1165619

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.17846	12	PG
B	0.06110	12	WW
C	-0.31202	9	PP

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 7 MSE= 0.008459
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 16.12121

Number of Means	2
Critical Range	0.0765954

PPCP Split Samples - SAS Analysis Results

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.09670	19	B
B	-0.12648	14	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	-0.03000366	0.12978441
PG	B	6	0.38692064	0.12731756
PP	A	3	-0.32219208	0.17379975
PP	B	6	-0.30693958	0.45237106
WW	A	5	-0.12483071	0.13704109
WW	B	7	0.19390900	0.34399533

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	0.18307899	0.02787274	0.0003	1
PP	-0.46422080	0.03773987	0.0001	2
WW	0.01877302	0.02920461	0.5408	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0001	0.0047
2	0.0001	.	0.0001
3	0.0047	0.0001	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	-0.31755387	0.03310621	0.0001	0.0001
B	0.14264134	0.02353591	0.0005	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	-0.03319374	0.04028444	0.4371	1
PG	B	0.39935172	0.04028444	0.0001	2
PP	A	-0.70143267	0.07315673	0.0001	3
PP	B	-0.22700893	0.04155023	0.0009	4
WW	A	-0.21803520	0.05375358	0.0048	5
WW	B	0.25558123	0.04044988	0.0004	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.0001	0.0001	0.0123	0.0284	0.0015
2	0.0001	.	0.0001	0.0001	0.0001	0.0399
3	0.0001	0.0001	.	0.0013	0.0011	0.0001
4	0.0123	0.0001	0.0013	.	0.8986	0.0001
5	0.0284	0.0001	0.0011	0.8986	.	0.0004
6	0.0015	0.0399	0.0001	0.0001	0.0004	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: T3CP
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.01419196	0.00709598	0.37	0.6953
Error	17	0.32486021	0.01910942		
Corrected Total	19	0.33905216			

R-Square	C.V.	Root MSE	LOGY Mean
0.041858	-85.45555	0.13824	-0.16176

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.01419196	0.00709598	0.37	0.6953

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.01419196	0.00709598	0.37	0.6953

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 17 MSE= 0.019109
Critical Value of T= 2.11
Least Significant Difference= 0.1602
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 6.631579

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	-0.13727	6	PG
A	-0.14684	7	PP
A	-0.19769	7	WW

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 17 MSE= 0.019109
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 6.631579

Number of Means	2	3
Critical Range	0.1601675	0.1947503

PPCP Split Samples - SAS Analysis Results

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.13727	6	PG
A	-0.14684	7	PP
A	-0.19769	7	WW

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.13726706	0.05643495	0.0263	1
PP	-0.14684142	0.05224861	0.0120	2
WW	-0.19768569	0.05224861	0.0015	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.9024	0.4429
2	0.9024	.	0.5007
3	0.4429	0.5007	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	27	4.00353415	0.14827904	17.42	0.0001
Error	12	0.10212493	0.00851041		
Corrected Total	39	4.10565907			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.975126	19.62945	0.09225	0.46997

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.88567677	0.44283838	52.03	0.0001
DATE(MILL)	22	2.88925684	0.13132986	15.43	0.0001
LAB	1	0.22145391	0.22145391	26.02	0.0003
MILL*LAB	2	0.00714663	0.00357331	0.42	0.6664

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.62630611	0.31315305	36.80	0.0001
DATE(MILL)	22	2.84908352	0.12950380	15.22	0.0001
LAB	1	0.22145391	0.22145391	26.02	0.0003
MILL*LAB	2	0.00714663	0.00357331	0.42	0.6664

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.62630611	0.31315305	2.42	0.1124

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 12 MSE= 0.00851
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 13.26316

Number of Means	2	3
Critical Range	0.0780519	0.0955681

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.59480	14	PP
A	0.55985	12	PG
B	0.26809	14	WW

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 12 MSE= 0.00851

Number of Means	2
Critical Range	0.0635612

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.55085	20	B
B	0.38908	20	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	0.49121198	0.14806792
PG	B	6	0.62847904	0.09957138
PP	A	7	0.52138341	0.34170603
PP	B	7	0.66822483	0.29686997
WW	A	7	0.16924747	0.37110479
WW	B	7	0.36693316	0.35031754

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	0.55579314	0.02795654	0.0001	1
PP	0.60355858	0.02613301	0.0001	2
WW	0.30660375	0.02613301	0.0001	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.2358	0.0001
2	0.2358	.	0.0001

3 0.0001 0.0001 .

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	0.40273444	0.02285354	0.0001	0.0003
B	0.57456920	0.02285354	0.0001	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	0.47343290	0.04040556	0.0001	1
PG	B	0.63815337	0.04040556	0.0001	2
PP	A	0.53451313	0.03916600	0.0001	3
PP	B	0.67260403	0.03916600	0.0001	4
WW	A	0.20025728	0.03916600	0.0003	5
WW	B	0.41295021	0.03916600	0.0001	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.0154	0.2991	0.0041	0.0004	0.3036
2	0.0154	.	0.0903	0.5518	0.0001	0.0018
3	0.2991	0.0903	.	0.0356	0.0001	0.0486
4	0.0041	0.5518	0.0356	.	0.0001	0.0005
5	0.0004	0.0001	0.0001	0.0001	.	0.0034
6	0.3036	0.0018	0.0486	0.0005	0.0034	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: DCG45
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.01127455	0.00563728	0.16	0.8537
Error	17	0.60007814	0.03529871		
Corrected Total	19	0.61135269			

R-Square	C.V.	Root MSE	LOGY Mean
0.018442	-207.3871	0.18788	-0.09059

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.01127455	0.00563728	0.16	0.8537

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.01127455	0.00563728	0.16	0.8537

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 17 MSE= 0.035299
Critical Value of T= 2.11
Least Significant Difference= 0.2177
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 6.631579

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	-0.0602	7	WW
A	-0.0977	7	PP
A	-0.1178	6	PG

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 17 MSE= 0.035299
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 6.631579

Number of Means	2	3
Critical Range	0.2176858	0.2646877

PPCP Split Samples - SAS Analysis Results

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.0602	7	WW
A	-0.0977	7	PP
A	-0.1178	6	PG

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.11777115	0.07670149	0.1431	1
PP	-0.09773738	0.07101178	0.1866	2
WW	-0.06015490	0.07101178	0.4087	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.8503	0.5887
2	0.8503	.	0.7129
3	0.5887	0.7129	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	27	6.93406592	0.25681726	36.66	0.0001
Error	12	0.08407304	0.00700609		
Corrected Total	39	7.01813896			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.988021	26.16125	0.08370	0.31995

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	4.70105283	2.35052642	335.50	0.0001
DATE(MILL)	22	2.14365202	0.09743873	13.91	0.0001
LAB	1	0.08613234	0.08613234	12.29	0.0043
MILL*LAB	2	0.00322873	0.00161436	0.23	0.7976

PPCP Split Samples - SAS Analysis Results

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	4.18565046	2.09282523	298.72	0.0001
DATE(MILL)	22	2.14530373	0.09751381	13.92	0.0001
LAB	1	0.08613234	0.08613234	12.29	0.0043
MILL*LAB	2	0.00322873	0.00161436	0.23	0.7976

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	4.18565046	2.09282523	21.46	0.0001

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 12 MSE= 0.007006
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 13.26316

Number of Means	2	3
Critical Range	0.0708184	0.0867113

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.83249	12	PG
B	0.18430	14	WW
C	0.01628	14	PP

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 12 MSE= 0.007006

Number of Means	2
Critical Range	0.0576706

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.36524	20	B
B	0.27465	20	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	0.77360536	0.20490232
PG	B	6	0.89137652	0.12034440
PP	A	7	-0.03259258	0.18552775
PP	B	7	0.06514480	0.22870452
WW	A	7	0.15421948	0.31378120
WW	B	7	0.21437438	0.37325783

PPCP Split Samples - SAS Analysis Results

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	0.81055901	0.02536565	0.0001	1
PP	0.00703282	0.02371111	0.7718	2
WW	0.15071116	0.02371111	0.0001	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0001	0.0001
2	0.0001	.	0.0011
3	0.0001	0.0011	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	0.26918522	0.02073557	0.0001	0.0043
B	0.37635010	0.02073557	0.0001	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	0.75973308	0.03666094	0.0001	1
PG	B	0.86138494	0.03666094	0.0001	2
PP	A	-0.06040736	0.03553626	0.1149	3
PP	B	0.07447300	0.03553626	0.0580	4
WW	A	0.10822994	0.03553626	0.0102	5
WW	B	0.19319237	0.03553626	0.0002	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.0789	0.0001	0.0001	0.0001	0.0001
2	0.0789	.	0.0001	0.0001	0.0001	0.0001
3	0.0001	0.0001	.	0.0256	0.0057	0.0003
4	0.0001	0.0001	0.0256	.	0.5145	0.0359
5	0.0001	0.0001	0.0057	0.5145	.	0.1345
6	0.0001	0.0001	0.0003	0.0359	0.1345	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: DCG46
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 9 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.37701373	0.18850686	1.01	0.4203
Error	6	1.12531348	0.18755225		
Corrected Total	8	1.50232721			

R-Square	C.V.	Root MSE	LOGY Mean
0.250953	-537.9088	0.43307	-0.08051

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.37701373	0.18850686	1.01	0.4203

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.37701373	0.18850686	1.01	0.4203

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 6 MSE= 0.187552
Critical Value of T= 2.45
Least Significant Difference= 1.117
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 1.8

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	0.4949	1	WW
A	-0.1109	2	PP
A	-0.1663	6	PG

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 6 MSE= 0.187552
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 1.8

Number of Means	2	3
Critical Range	1.1170133	1.4006076

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.4949	1	WW
A	-0.1109	2	PP
A	-0.1663	6	PG

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.16626596	0.17680132	0.3833	1
PP	-0.11092437	0.30622887	0.7296	2
WW	0.49485002	0.43307303	0.2967	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.8808	0.2073
2	0.8808	.	0.2969
3	0.2073	0.2969	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 25 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	20	3.05539668	0.15276983	1.47	0.3877
Error	4	0.41704623	0.10426156		
Corrected Total	24	3.47244291			

R-Square	C.V.	Root MSE	LOGVAL Mean

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.51635771	0.25817885	2.48	0.1996
DATE(MILL)	15	2.39133216	0.15942214	1.53	0.3670
LAB	1	0.00219924	0.00219924	0.02	0.8915
MILL*LAB	2	0.14550757	0.07275378	0.70	0.5496

PPCP Split Samples - SAS Analysis Results

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.64524856	0.32262428	3.09	0.1541
DATE(MILL)	15	2.45529386	0.16368626	1.57	0.3559
LAB	1	0.06195868	0.06195868	0.59	0.4838
MILL*LAB	2	0.14550757	0.07275378	0.70	0.5496

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.64524856	0.32262428	1.97	0.1738

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 4 MSE= 0.104262
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 7.636364

Number of Means	2	3
Critical Range	0.4588014	0.5889406

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.0537	12	PG
A	0.0436	6	PP
A	-0.2696	7	WW

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 4 MSE= 0.104262
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 12.48

Number of Means	2
Critical Range	0.3588895

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.00778	12	B
A	-0.08269	13	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	-0.02942096	0.48661957
PG	B	6	0.13684499	0.06581861
PP	A	3	0.04912237	0.32884227
PP	B	3	0.03798112	0.30813431
WW	A	4	-0.26143937	0.62306391
WW	B	3	-0.28054584	0.21896655

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	0.01164701	0.09785214	0.9110	1
PP	-0.01933824	0.13699299	0.8946	2
WW	-0.38088917	0.13182157	0.0446	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.8629	0.0751
2	0.8629	.	0.1300
3	0.0751	0.1300	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	-0.04250538	0.12606428	0.7529	0.4838
B	-0.21654822	0.14054801	0.1982	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	-0.03168542	0.14142559	0.8337	1
PG	B	0.05497944	0.14142559	0.7173	2
PP	A	0.03763343	0.26626652	0.8944	3
PP	B	-0.07630992	0.26626652	0.7887	4
WW	A	-0.13346416	0.22832166	0.5902	5
WW	B	-0.62831418	0.29476199	0.1000	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.6931	0.8294	0.8895	0.7240	0.1421
2	0.6931	.	0.9569	0.6857	0.5216	0.1048
3	0.8294	0.9569	.	0.8152	0.6512	0.1689
4	0.8895	0.6857	0.8152	.	0.8785	0.2370
5	0.7240	0.5216	0.6512	0.8785	.	0.3395
6	0.1421	0.1048	0.1689	0.2370	0.3395	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

Split Sample Analysis: T3CG345
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 19 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.00653189	0.00326595	0.20	0.8241
Error	16	0.26692205	0.01668263		
Corrected Total	18	0.27345394			

R-Square	C.V.	Root MSE	LOGY Mean
0.023887	-55.53958	0.12916	-0.23256

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.00653189	0.00326595	0.20	0.8241

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.00653189	0.00326595	0.20	0.8241

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 16 MSE= 0.016683
Critical Value of T= 2.12
Least Significant Difference= 0.1543
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 6.3

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	-0.21725	7	WW
A	-0.22338	6	PG
A	-0.25959	6	PP

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 16 MSE= 0.016683
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 6.3

Number of Means	2	3
Critical Range	0.154274	0.1877813

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.21725	7	WW
A	-0.22338	6	PG
A	-0.25959	6	PP

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.22338350	0.05272986	0.0006	1
PP	-0.25959386	0.05272986	0.0002	2
WW	-0.21724583	0.04881836	0.0004	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.6338	0.9330
2	0.6338	.	0.5639
3	0.9330	0.5639	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 39 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	27	19.1457895	0.7091033	173.89	0.0001
Error	11	0.0448556	0.0040778		
Corrected Total	38	19.1906451			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.997663	13.05618	0.06386	0.48910

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	11.1696934	5.5848467	1369.58	0.0001
DATE(MILL)	22	7.5240515	0.3420023	83.87	0.0001
LAB	1	0.4244599	0.4244599	104.09	0.0001
MILL*LAB	2	0.0275847	0.0137923	3.38	0.0716

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	11.9433431	5.9716716	1464.44	0.0001
DATE(MILL)	22	7.5653456	0.3438793	84.33	0.0001
LAB	1	0.4426287	0.4426287	108.55	0.0001
MILL*LAB	2	0.0275847	0.0137923	3.38	0.0716

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	11.9433431	5.9716716	17.37	0.0001

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 11 MSE= 0.004078
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 12.94862

Number of Means	2	3
Critical Range	0.055237	0.0677811

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.99296	12	PG
B	0.74766	14	WW
C	-0.25445	13	PP

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 11 MSE= 0.004078
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 19.48718

Number of Means	2
Critical Range	0.0450264

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.56986	20	B
B	0.40408	19	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	0.88126759	0.09475873
PG	B	6	1.10465109	0.05198391
PP	A	6	-0.34720505	0.68332577
PP	B	7	-0.17494817	0.62924356
WW	A	7	0.63903223	0.50010770
WW	B	7	0.85627806	0.47272120

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	0.99151315	0.01935175	0.0001	1
PP	-0.35388523	0.01893921	0.0001	2
WW	0.78891950	0.01808948	0.0001	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0001	0.0001
2	0.0001	.	0.0001
3	0.0001	0.0001	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	0.34908870	0.01666321	0.0001	0.0001
B	0.60194291	0.01588997	0.0001	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	0.89014146	0.02796906	0.0001	1
PG	B	1.09288484	0.02796906	0.0001	2
PP	A	-0.52656922	0.03133190	0.0001	3
PP	B	-0.18120125	0.02747989	0.0001	4
WW	A	0.68369386	0.02711102	0.0001	5
WW	B	0.89414514	0.02711102	0.0001	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.0004	0.0001	0.0001	0.0003	0.9200
2	0.0004	.	0.0001	0.0001	0.0001	0.0003
3	0.0001	0.0001	.	0.0001	0.0001	0.0001
4	0.0001	0.0001	0.0001	.	0.0001	0.0001
5	0.0003	0.0001	0.0001	0.0001	.	0.0003
6	0.9200	0.0003	0.0001	0.0001	0.0003	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: T3CG346
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 10 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.42256445	0.21128223	0.44	0.6631
Error	7	3.39251807	0.48464544		
Corrected Total	9	3.81508252			

R-Square	C.V.	Root MSE	LOGY Mean
0.110762	488.3481	0.69616	0.14256

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.42256445	0.21128223	0.44	0.6631

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.42256445	0.21128223	0.44	0.6631

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 7 MSE= 0.484645
Critical Value of T= 2.36
Least Significant Difference= 1.6462
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 2

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	0.5563	1	PP
A	0.2102	6	WW
A	-0.1306	3	PG

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 7 MSE= 0.484645
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 2

Number of Means	2	3
Critical Range	1.6459892	2.0501897

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.5563	1	PP
A	0.2102	6	WW
A	-0.1306	3	PG

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.13064988	0.40193094	0.7546	1
PP	0.55630250	0.69616481	0.4505	2
WW	0.21019958	0.28420809	0.4836	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.4211	0.5110
2	0.4211	.	0.6593
3	0.5110	0.6593	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 27 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	22	6.19191557	0.28145071	0.86	0.6449
Error	4	1.30646599	0.32661650		
Corrected Total	26	7.49838155			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.825767	-603.1986	0.57150	-0.09475

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.08543883	0.04271942	0.13	0.8810
DATE(MILL)	17	5.88847021	0.34638060	1.06	0.5369
LAB	1	0.14515670	0.14515670	0.44	0.5415
MILL*LAB	2	0.07284983	0.03642491	0.11	0.8972

PPCP Split Samples - SAS Analysis Results

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.21157789	0.10578895	0.32	0.7407
DATE(MILL)	17	5.65516794	0.33265694	1.02	0.5565
LAB	1	0.20108681	0.20108681	0.62	0.4765
MILL*LAB	2	0.07284983	0.03642491	0.11	0.8972

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.21157789	0.10578895	0.32	0.7318

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 4 MSE= 0.326616
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 7.731278

Number of Means	2	3
Critical Range	0.807048	1.0359675

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.0659	9	PG
A	-0.0694	13	WW
A	-0.2127	5	PP

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 4 MSE= 0.326616
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 13.03704

Number of Means	2
Critical Range	0.621492

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.0162	11	A
A	-0.1710	16	B

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	3	-0.11950863	0.85569874
PG	B	6	-0.03903041	0.10053238
PP	A	2	-0.07133375	1.31333240
PP	B	3	-0.30693958	0.53382796
WW	A	6	0.11327189	0.66604539
WW	B	7	-0.22593802	0.39450191

PPCP Split Samples - SAS Analysis Results

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.08665341	0.23450278	0.7305	1
PP	-0.34112906	0.28575186	0.2985	2
WW	-0.08557908	0.16949972	0.6402	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.5290	0.9972
2	0.5290	.	0.4847
3	0.9972	0.4847	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	-0.03129882	0.26074281	0.9102	0.4765
B	-0.31094222	0.17964447	0.1585	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	-0.02133770	0.45457115	0.9648	1
PG	B	-0.15196913	0.25817906	0.5877	2
PP	A	-0.06297781	0.57150372	0.9176	3
PP	B	-0.61928031	0.40411415	0.2002	4
WW	A	-0.00958096	0.28041023	0.9744	5
WW	B	-0.16157720	0.24593604	0.5471	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.8304	0.9573	0.3812	0.9835	0.7996
2	0.8304	.	0.8940	0.3850	0.7277	0.9798
3	0.9573	0.8940	.	0.5291	0.9372	0.8818
4	0.3812	0.3850	0.5291	.	0.2829	0.3881
5	0.9835	0.7277	0.9372	0.2829	.	0.7259
6	0.7996	0.9798	0.8818	0.3881	0.7259	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: T3CG456
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 16 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.05414557	0.02707278	1.10	0.3629
Error	13	0.32084589	0.02468045		
Corrected Total	15	0.37499145			

R-Square	C.V.	Root MSE	LOGY Mean
0.144391	-65.36289	0.15710	-0.24035

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.05414557	0.02707278	1.10	0.3629

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.05414557	0.02707278	1.10	0.3629

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 13 MSE= 0.02468
Critical Value of T= 2.16
Least Significant Difference= 0.2222
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 4.666667

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	-0.1256	3	PP
A	-0.2478	7	WW
A	-0.2891	6	PG

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 13 MSE= 0.02468
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 4.666667

Number of Means	2	3
Critical Range	0.2221894	0.2715589

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.1256	3	PP
A	-0.2478	7	WW
A	-0.2891	6	PG

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.28907727	0.06413586	0.0006	1
PP	-0.12558357	0.09070181	0.1895	2
WW	-0.24777085	0.05937827	0.0011	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.1649	0.6443
2	0.1649	.	0.2801
3	0.6443	0.2801	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 34 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	24	8.60874368	0.35869765	39.36	0.0001
Error	9	0.08201955	0.00911328		
Corrected Total	33	8.69076324			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.990562	34.00536	0.09546	0.28073

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	3.07395743	1.53697872	168.65	0.0001
DATE(MILL)	19	5.17613212	0.27242801	29.89	0.0001
LAB	1	0.35454466	0.35454466	38.90	0.0002
MILL*LAB	2	0.00410947	0.00205474	0.23	0.8025

PPCP Split Samples - SAS Analysis Results

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	3.65536980	1.82768490	200.55	0.0001
DATE(MILL)	19	5.02820643	0.26464244	29.04	0.0001
LAB	1	0.26945378	0.26945378	29.57	0.0004
MILL*LAB	2	0.00410947	0.00205474	0.23	0.8025

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	3.65536980	1.82768490	6.91	0.0056

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 9 MSE= 0.009113
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 10.7234

Number of Means	2	3
Critical Range	0.0932582	0.1151073

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.55683	12	PG
B	0.33780	14	WW
C	-0.23328	8	PP

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 9 MSE= 0.009113
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 16.94118

Number of Means	2
Critical Range	0.0741962

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.33313	18	B
B	0.22179	16	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	0.41228803	0.14538937
PG	B	6	0.70136530	0.05907703
PP	A	3	-0.14083607	0.66171733
PP	B	5	-0.28873950	0.66290201
WW	A	7	0.21390971	0.43422660
WW	B	7	0.46168057	0.45134480

PPCP Split Samples - SAS Analysis Results

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	0.55572982	0.02892982	0.0001	1
PP	-0.39055449	0.03897282	0.0001	2
WW	0.38291724	0.02704280	0.0001	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0001	0.0018
2	0.0001	.	0.0001
3	0.0018	0.0001	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	0.06662561	0.03110374	0.0608	0.0004
B	0.29876944	0.02509808	0.0001	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	0.42362868	0.04181223	0.0001	1
PG	B	0.68783097	0.04181223	0.0001	2
PP	A	-0.48474217	0.07291147	0.0001	3
PP	B	-0.29636681	0.04773176	0.0002	4
WW	A	0.26099033	0.04052951	0.0001	5
WW	B	0.50484416	0.04052951	0.0001	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.0018	0.0001	0.0001	0.0210	0.1966
2	0.0018	.	0.0001	0.0001	0.0001	0.0119
3	0.0001	0.0001	.	0.0799	0.0001	0.0001
4	0.0001	0.0001	0.0799	.	0.0001	0.0001
5	0.0210	0.0001	0.0001	0.0001	.	0.0029
6	0.1966	0.0119	0.0001	0.0001	0.0029	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: T4CG
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 17 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.06190982	0.03095491	1.05	0.3769
Error	14	0.41392886	0.02956635		
Corrected Total	16	0.47583868			

R-Square	C.V.	Root MSE	LOGY Mean
0.130107	-86.44157	0.17195	-0.19892

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.06190982	0.03095491	1.05	0.3769

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.06190982	0.03095491	1.05	0.3769

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 14 MSE= 0.029566
Critical Value of T= 2.14
Least Significant Difference= 0.2252
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 5.361702

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	-0.1329	4	PP
A	-0.1685	7	WW
A	-0.2785	6	PG

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 14 MSE= 0.029566
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 5.361702

Number of Means	2	3
Critical Range	0.2252397	0.2748608

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.1329	4	PP
A	-0.1685	7	WW
A	-0.2785	6	PG

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.27847127	0.07019775	0.0014	1
PP	-0.13286973	0.08597434	0.1445	2
WW	-0.16847371	0.06499049	0.0213	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.2107	0.2695
2	0.2107	.	0.7460
3	0.2695	0.7460	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 35 observations can be used in this analysis.

General Linear Models Procedure

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	25	6.13584484	0.24543379	17.37	0.0001
Error	9	0.12714639	0.01412738		
Corrected Total	34	6.26299123			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.979699	547.7218	0.11886	0.02170

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	1.41902932	0.70951466	50.22	0.0001
DATE(MILL)	20	4.34944253	0.21747213	15.39	0.0001
LAB	1	0.34412264	0.34412264	24.36	0.0008
MILL*LAB	2	0.02325035	0.01162518	0.82	0.4697

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	2.12399622	1.06199811	75.17	0.0001
DATE(MILL)	20	4.37269728	0.21863486	15.48	0.0001
LAB	1	0.29948117	0.29948117	21.20	0.0013
MILL*LAB	2	0.02325035	0.01162518	0.82	0.4697

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	2.12399622	1.06199811	4.86	0.0191

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 9 MSE= 0.014127
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 11.28358

Number of Means	2	3
Critical Range	0.113194	0.1397138

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.15572	12	PG
A	0.12640	14	WW
B	-0.31987	9	PP

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 9 MSE= 0.014127
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 17.48571

Number of Means	2
Critical Range	0.0909296

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.10051	18	B
B	-0.06174	17	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	0.01648675	0.20756239
PG	B	6	0.29495802	0.07946525
PP	A	4	-0.36092437	0.44904227
PP	B	5	-0.28701947	0.48865869
WW	A	7	0.04216640	0.49425683
WW	B	7	0.21064010	0.45222676

PPCP Split Samples - SAS Analysis Results

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	0.16152611	0.03601961	0.0015	1
PP	-0.43650789	0.04244951	0.0001	2
WW	0.16807512	0.03367014	0.0007	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0001	0.8973
2	0.0001	.	0.0001
3	0.8973	0.0001	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	-0.15800409	0.03590028	0.0017	0.0013
B	0.08673298	0.03262799	0.0261	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	0.01092437	0.05205910	0.8385	1
PG	B	0.31212785	0.05205910	0.0002	2
PP	A	-0.56937762	0.07964235	0.0001	3
PP	B	-0.30363817	0.06576251	0.0013	4
WW	A	0.08444097	0.05046203	0.1286	5
WW	B	0.25170926	0.05046203	0.0008	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.0031	0.0002	0.0046	0.3371	0.0089
2	0.0031	.	0.0001	0.0001	0.0119	0.4262
3	0.0002	0.0001	.	0.0522	0.0001	0.0001
4	0.0046	0.0001	0.0522	.	0.0011	0.0001
5	0.3371	0.0119	0.0001	0.0011	.	0.0531
6	0.0089	0.4262	0.0001	0.0001	0.0531	.

Split Sample Analysis: DCC35 General Linear Models -

Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 10 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.03479233	0.01739616	0.10	0.9045
Error	7	1.19523217	0.17074745		
Corrected Total	9	1.23002450			

R-Square	C.V.	Root MSE	LOGY Mean
0.028286	-1832.581	0.41322	-0.02255

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.03479233	0.01739616	0.10	0.9045

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.03479233	0.01739616	0.10	0.9045

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 7 MSE= 0.170747
Critical Value of T= 2.36
Least Significant Difference= 0.7638
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 3.272727

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	0.04165	3	PP
A	0.00706	3	WW
A	-0.09290	4	PG

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 7 MSE= 0.170747
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 3.272727

Number of Means	2	3
Critical Range	0.7637516	0.9513037

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.04165	3	PP
A	0.00706	3	WW
A	-0.09290	4	PG

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.09290277	0.20660799	0.6666	1
PP	0.04164625	0.23857036	0.8664	2
WW	0.00706310	0.23857036	0.9772	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.6827	0.7607
2	0.6827	.	0.9212
3	0.7607	0.9212	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 30 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	27	3.25965317	0.12072790	3.41	0.2519
Error	2	0.07083779	0.03541889		
Corrected Total	29	3.33049096			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.978731	-57.12172	0.18820	-0.32947

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	1.09999728	0.54999864	15.53	0.0605
DATE(MILL)	22	2.00822324	0.09128287	2.58	0.3170
LAB	1	0.11646322	0.11646322	3.29	0.2115
MILL*LAB	2	0.03496944	0.01748472	0.49	0.6695

PPCP Split Samples - SAS Analysis Results

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.75473694	0.37736847	10.65	0.0858
DATE(MILL)	22	2.07230496	0.09419568	2.66	0.3091
LAB	1	0.04878101	0.04878101	1.38	0.3614
MILL*LAB	2	0.03496944	0.01748472	0.49	0.6695

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.75473694	0.37736847	4.01	0.0328

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 2 MSE= 0.035419

Number of Means	2	3
Critical Range	0.3621331	0.495796

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.06904	10	PG
A	-0.39542	10	WW
A	-0.52396	10	PP

Alpha= 0.05 df= 2 MSE= 0.035419
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 14.4

Number of Means	2
Critical Range	0.3017776

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	-0.32150	18	B
A	-0.34142	12	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	4	-0.11713027	0.28705633
PG	B	6	-0.03697479	0.29221448
PP	A	5	-0.55917600	0.19446304
PP	B	5	-0.48873950	0.35736155
WW	A	3	-0.27756089	0.21245150
WW	B	7	-0.44592546	0.34559811

PPCP Split Samples - SAS Analysis Results

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.10628212	0.06676436	0.2524	1
PP	-0.51429479	0.06096554	0.0138	2
WW	-0.42213988	0.08494092	0.0382	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0458	0.0998
2	0.0458	.	0.4711
3	0.0998	0.4711	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

Least Squares Means

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	-0.42709247	0.09178855	0.0432	0.3614
B	-0.26805205	0.06463257	0.0535	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	-0.25679711	0.11719154	0.1598	1
PG	B	0.04423288	0.08359067	0.6496	2
PP	A	-0.60234042	0.14637706	0.0543	3
PP	B	-0.42624916	0.14637706	0.1005	4
WW	A	-0.42213988	0.20165847	0.1714	5

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
WW	B	-0.42213988	0.09582628	0.0479	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.1892	0.2067	0.4615	0.5519	0.3888
2	0.1892	.	0.0617	0.1080	0.1661	0.0670
3	0.2067	0.0617	.	0.5762	0.5447	0.4113
4	0.4615	0.1080	0.5762	.	0.9883	0.9834
5	0.5519	0.1661	0.5447	0.9883	.	1.0000
6	0.3888	0.0670	0.4113	0.9834	1.0000	.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: DCC45
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 14 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.15437563	0.07718782	12.61	0.0014
Error	11	0.06733991	0.00612181		
Corrected Total	13	0.22171554			

R-Square	C.V.	Root MSE	LOGY Mean
0.696278	-46.06485	0.07824	-0.16985

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.15437563	0.07718782	12.61	0.0014

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.15437563	0.07718782	12.61	0.0014

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 11 MSE= 0.006122
Critical Value of T= 2.20
Least Significant Difference= 0.1284
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 3.6

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	-0.07399	6	PG
A	-0.19264	6	WW
B	-0.38908	2	PP

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 11 MSE= 0.006122
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 3.6

Number of Means	2	3
Critical Range	0.1283566	0.157506

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.07399	6	PG
A	-0.19264	6	WW
B	-0.38908	2	PP

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.07398649	0.03194216	0.0408	1
PP	-0.38907563	0.05532544	0.0001	2
WW	-0.19264258	0.03194216	0.0001	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0004	0.0235
2	0.0004	.	0.0106
3	0.0235	0.0106	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 34 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	26	13.1368608	0.5052639	193.40	0.0001
Error	7	0.0182878	0.0026125		
Corrected Total	33	13.1551486			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.998610	8.422941	0.05111	0.60683

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	9.94310008	4.97155004	1902.95	0.0001
DATE(MILL)	21	2.98423244	0.14210631	54.39	0.0001
LAB	1	0.13876700	0.13876700	53.12	0.0002
MILL*LAB	2	0.07076129	0.03538065	13.54	0.0039

PPCP Split Samples - SAS Analysis Results

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	7.36116184	3.68058092	1408.81	0.0001
DATE(MILL)	21	3.06187399	0.14580352	55.81	0.0001
LAB	1	0.19662418	0.19662418	75.26	0.0001
MILL*LAB	2	0.07076129	0.03538065	13.54	0.0039

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	7.36116184	3.68058092	25.24	0.0001

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 7 MSE= 0.002613
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 11.05512

Number of Means 2 3
Critical Range 0.051402 0.0640247

SNK Grouping	Mean	N	MILL
A	1.28816	12	PG
B	0.44010	13	WW
C	-0.06077	9	PP

Alpha= 0.05 df= 7 MSE= 0.002613
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 16.47059

Number of Means 2
Critical Range 0.0421122

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.67352	14	A
B	0.56015	20	B

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	1.25116699	0.27691116
PG	B	6	1.32515349	0.29065402
PP	A	2	-0.05395270	0.23744087
PP	B	7	-0.06271399	0.29380726
WW	A	6	0.33835499	0.43936191
WW	B	7	0.52730506	0.34996553

PPCP Split Samples - SAS Analysis Results

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	1.30294676	0.01548961	0.0001	1
PP	-0.21955229	0.02857309	0.0001	2
WW	0.44841402	0.01515940	0.0001	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0001	0.0001
2	0.0001	.	0.0001
3	0.0001	0.0001	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	0.38474906	0.02329918	0.0001	0.0001
B	0.63645660	0.01280122	0.0001	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	1.26454247	0.02238711	0.0001	1
PG	B	1.34135105	0.02238711	0.0001	2
PP	A	-0.45811292	0.06128245	0.0001	3
PP	B	0.01900834	0.02213262	0.4189	4
WW	A	0.34781764	0.02507881	0.0001	5

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
WW	B	0.54901040	0.02199557	0.0001	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.0492	0.0001	0.0001	0.0001	0.0001
2	0.0492	.	0.0001	0.0001	0.0001	0.0001
3	0.0001	0.0001	.	0.0003	0.0001	0.0001
4	0.0001	0.0001	0.0003	.	0.0001	0.0001
5	0.0001	0.0001	0.0001	0.0001	.	0.0008
6	0.0001	0.0001	0.0001	0.0001	0.0008	.

Split Sample Analysis: T3CC345
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 16 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.18192958	0.09096479	2.61	0.1118
Error	13	0.45389206	0.03491477		
Corrected Total	15	0.63582164			

R-Square	C.V.	Root MSE	LOGY Mean
0.286133	1290.750	0.18685	0.01448

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.18192958	0.09096479	2.61	0.1118

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.18192958	0.09096479	2.61	0.1118

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 13 MSE= 0.034915
Critical Value of T= 2.16
Least Significant Difference= 0.2643
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 4.666667

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	0.2354	3	PP
B A	-0.0244	6	PG
B	-0.0469	7	WW

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 13 MSE= 0.034915
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 4.666667

Number of Means	2	3
Critical Range	0.2642721	0.3229922

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.2354	3	PP
A	-0.0244	6	PG
A	-0.0469	7	WW

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.02435820	0.07628322	0.7546	1
PP	0.23544370	0.10788076	0.0480	2
WW	-0.04693693	0.07062453	0.5179	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0710	0.8314
2	0.0710	.	0.0474
3	0.8314	0.0474	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 34 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	25	9.52572867	0.38102915	308.04	0.0001
Error	8	0.00989574	0.00123697		
Corrected Total	33	9.53562441			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.998962	5.786973	0.03517	0.60775

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	7.27844160	3.63922080	2942.05	0.0001
DATE(MILL)	20	2.23797132	0.11189857	90.46	0.0001
LAB	1	0.00679522	0.00679522	5.49	0.0471
MILL*LAB	2	0.00252053	0.00126027	1.02	0.4035

PPCP Split Samples - SAS Analysis Results

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	7.31431510	3.65715755	2956.55	0.0001
DATE(MILL)	20	2.20845595	0.11042280	89.27	0.0001
LAB	1	0.00095023	0.00095023	0.77	0.4063
MILL*LAB	2	0.00252053	0.00126027	1.02	0.4035

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	7.31431510	3.65715755	33.12	0.0001

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 8 MSE= 0.001237
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 10.7234

Number of Means	2	3
Critical Range	0.0350246	0.0434013

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	1.05001	12	PG
B	0.67448	14	WW
C	-0.17239	8	PP

Alpha= 0.05 df= 8 MSE= 0.001237

Number of Means	2
Critical Range	0.0278173

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	0.60804	17	A
A	0.60747	17	B

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	1.03783041	0.10385793
PG	B	6	1.06218860	0.11542734
PP	A	4	-0.11183295	0.35984020
PP	B	4	-0.23295353	0.26404027
WW	A	7	0.65100708	0.34268094
WW	B	7	0.69794401	0.36414601

PPCP Split Samples - SAS Analysis Results

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	1.04882976	0.01065828	0.0001	1
PP	-0.21559737	0.01280966	0.0001	2
WW	0.69247795	0.00996307	0.0001	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0001	0.0001
2	0.0001	.	0.0001
3	0.0001	0.0001	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	0.49997321	0.01175125	0.0001	0.4063
B	0.51716701	0.01175125	0.0001	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	1.02672886	0.01540441	0.0001	1
PG	B	1.07093067	0.01540441	0.0001	2
PP	A	-0.19950503	0.02797447	0.0001	3
PP	B	-0.23168972	0.02797447	0.0001	4
WW	A	0.67269582	0.01493183	0.0001	5

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
WW	B	0.71226009	0.01493183	0.0001	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.0821	0.0001	0.0001	0.0001	0.0001
2	0.0821	.	0.0001	0.0001	0.0001	0.0001
3	0.0001	0.0001	.	0.5357	0.0001	0.0001
4	0.0001	0.0001	0.5357	.	0.0001	0.0001
5	0.0001	0.0001	0.0001	0.0001	.	0.1132
6	0.0001	0.0001	0.0001	0.0001	0.1132	.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: T4CC
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 11 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.04900754	0.04900754	1.20	0.3015
Error	9	0.36705549	0.04078394		
Corrected Total	10	0.41606303			

R-Square	C.V.	Root MSE	LOGY Mean
0.117789	410.0871	0.20195	0.04925

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	1	0.04900754	0.04900754	1.20	0.3015

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	1	0.04900754	0.04900754	1.20	0.3015

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experiment-wise error rate.

Alpha= 0.05 df= 9 MSE= 0.040784
Critical Value of T= 2.26
Least Significant Difference= 0.2766
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 5.454545

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	0.1224	5	WW
A	-0.0117	6	PG

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 9 MSE= 0.040784
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 5.454545

Number of Means 2
Critical Range 0.2766186

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	0.1224	5	WW
A	-0.0117	6	PG

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
PG	-0.01168614	0.08244589	0.8904	0.3015
WW	0.12236397	0.09031494	0.2085	

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 26 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	19	1.16613687	0.06137562	2.07	0.1866
Error	6	0.17752761	0.02958794		
Corrected Total	25	1.34366449			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.867878	-141.6087	0.17201	-0.12147

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.38652087	0.19326043	6.53	0.0312
DATE(MILL)	15	0.74118359	0.04941224	1.67	0.2728
LAB	1	0.01035329	0.01035329	0.35	0.5758
MILL*LAB	1	0.02807913	0.02807913	0.95	0.3676

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.38871992	0.19435996	6.57	0.0308
DATE(MILL)	14	0.77115712	0.05508265	1.86	0.2284
LAB	1	0.01971557	0.01971557	0.67	0.4455
MILL*LAB	1	0.02807913	0.02807913	0.95	0.3676

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.38871992	0.19435996	3.53	0.0574

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 6 MSE= 0.029588
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 4.5

Number of Means 2 3
Critical Range 0.280598 0.3518379

Means with the same letter are not significantly different.

General Linear Models Procedure

SNK Grouping	Mean	N	MILL
A	-0.0485	12	PG
A	-0.1275	12	WW
B	-0.5229	2	PP

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 6 MSE= 0.029588

Number of Means 2
Critical Range 0.1650894

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	LAB
A	-0.11221	13	A
A	-0.13073	13	B

General Linear Models Procedure

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	-0.05438227	0.26472182
PG	B	6	-0.04269613	0.07246449
PP	A	1	-0.52287875	.
PP	B	1	-0.52287875	.
WW	A	6	-0.10159914	0.27435103
WW	B	6	-0.15339745	0.19783760

PPCP Split Samples - SAS Analysis Results

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.04814181	0.05212734	0.3914	1
PP	-0.52287875	0.12163046	0.0051	2
WW	-0.15850573	0.05234141	0.0231	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.0115	0.1858
2	0.0115	.	0.0332
3	0.1858	0.0332	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN
A	Non-est
B	Non-est

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	-0.05515350	0.07533958	0.4917	1
PG	B	-0.04113013	0.07533958	0.6048	2
PP	A	Non-est	.	.	3
PP	B	Non-est	.	.	4
WW	A	-0.07898552	0.08758394	0.4019	5
WW	B	-0.23802594	0.08758394	0.0347	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.9016	.	.	0.8434	0.1645
2	0.9016	.	.	.	0.7543	0.1392
3	.	.	.	.	.	.
4	.	.	.	.	.	.
5	0.8434	0.7543	.	.	.	0.3007
6	0.1645	0.1392	.	.	0.3007	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

PPCP Split Samples - SAS Analysis Results

Split Sample Analysis: T3CV345
General Linear Models - Model A
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW

Number of observations in data set = 20

NOTE: Due to missing values, only 11 observations can be used in this analysis.

Dependent Variable: LOGY

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.00190893	0.00095447	0.02	0.9846
Error	8	0.49031815	0.06128977		
Corrected Total	10	0.49222708			

R-Square	C.V.	Root MSE	LOGY Mean
0.003878	-172.0513	0.24757	-0.14389

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.00190893	0.00095447	0.02	0.9846

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.00190893	0.00095447	0.02	0.9846

T tests (LSD) for variable: LOGY

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 8 MSE= 0.06129
Critical Value of T= 2.31
Least Significant Difference= 0.5548
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 2.117647

Means with the same letter are not significantly different.

T Grouping	Mean	N	MILL
A	-0.1287	4	WW
A	-0.1326	1	PP
A	-0.1559	6	PG

Student-Newman-Keuls test for variable: LOGY

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 8 MSE= 0.06129
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 2.117647

Number of Means	2	3
Critical Range	0.5547893	0.6874747

Means with the same letter are not significantly different.

SNK Grouping	Mean	N	MILL
A	-0.1287	4	WW
A	-0.1326	1	PP
A	-0.1559	6	PG

Least Squares Means

MILL	LOGY LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.15587911	0.10106909	0.1616	1
PP	-0.13262557	0.24756770	0.6067	2
WW	-0.12872745	0.12378385	0.3288	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.9328	0.8693
2	0.9328	.	0.9891
3	0.8693	0.9891	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

General Linear Models - Model B
Class Level Information

Class	Levels	Values
MILL	3	PG PP WW
SET	7	1 2 3 4 5 6 7
LAB	2	A B
DATE	18	02MAR92 03MAR92 09MAR92 10FEB92 10MAR92 11FEB92 11MAR92 16MAR92 17MAR92 18MAR92 20FEB92 23MAR92 24FEB92 24MAR92 25FEB92 25MAR92 26FEB92 31MAR92

Number of observations in data set = 40

NOTE: Due to missing values, only 25 observations can be used in this analysis.

Dependent Variable: LOGVAL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	18	1.85946499	0.10330361	2.72	0.1104
Error	6	0.22818447	0.03803075		
Corrected Total	24	2.08764947			

R-Square	C.V.	Root MSE	LOGVAL Mean
0.890698	-215.6484	0.19501	-0.09043

Source	DF	Type I SS	Mean Square	F Value	Pr > F
MILL	2	0.45507397	0.22753699	5.98	0.0372
DATE(MILL)	13	1.30516727	0.10039748	2.64	0.1203
LAB	1	0.09790866	0.09790866	2.57	0.1597
MILL*LAB	2	0.00131509	0.00065754	0.02	0.9829

PPCP Split Samples - SAS Analysis Results

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.43250440	0.21625220	5.69	0.0412
DATE(MILL)	13	1.29344161	0.09949551	2.62	0.1225
LAB	1	0.06320581	0.06320581	1.66	0.2448
MILL*LAB	2	0.00131509	0.00065754	0.02	0.9829

Tests of Hypotheses using the Type III MS for DATE(MILL) as an error term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
MILL	2	0.43250440	0.21625220	2.17	0.1533

Student-Newman-Keuls test for variable: LOGVAL

NOTE: This test controls the type I experimentwise error rate
under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 6 MSE= 0.038031
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 4.449438

Number of Means 2 3
Critical Range 0.3199251 0.4011497

Means with the same letter are not significantly different.

General Linear Models Procedure

SNK Grouping		Mean	N	MILL
	A	0.2124	2	PP
B	A	-0.0158	12	PG
B		-0.2269	11	WW

NOTE: This test controls the type I experimentwise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha= 0.05 df= 6 MSE= 0.038031
WARNING: Cell sizes are not equal.
Harmonic Mean of cell sizes= 12.32

Number of Means 2
Critical Range 0.1922629

Means with the same letter are not significantly different.

SNK Grouping		Mean	N	LAB
	A	-0.04742	14	B
	A	-0.14518	11	A

Level of MILL	Level of LAB	N	LOGVAL Mean	LOGVAL SD
PG	A	6	-0.09376638	0.43360729
PG	B	6	0.06211273	0.17061383
PP	A	1	0.14612804	.
PP	B	1	0.27875360	.
WW	A	4	-0.29511402	0.30645240
WW	B	7	-0.18789975	0.16034602

Least Squares Means

MILL	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	-0.03833638	0.05909839	0.5406	1
PP	0.21244082	0.13789624	0.1743	2
WW	-0.25650710	0.06894812	0.0098	3

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3
1	.	0.1456	0.0531
2	0.1456	.	0.0228
3	0.0531	0.0228	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	Pr > |T| HO: LSMEAN1=LSMEAN2
A	-0.10084466	0.08244364	0.2671	0.2448
B	0.04590955	0.07576638	0.5668	

MILL	LAB	LOGVAL LSMEAN	Std Err LSMEAN	Pr > |T| HO:LSMEAN=0	LSMEAN Number
PG	A	-0.10633660	0.08541484	0.2596	1
PG	B	0.02966383	0.08541484	0.7402	2
PP	A	0.14612804	0.19501473	0.4820	3
PP	B	0.27875360	0.19501473	0.2028	4
WW	A	-0.34232540	0.12588147	0.0347	5
WW	B	-0.17068880	0.07961443	0.0757	6

Pr > |T| HO: LSMEAN(i)=LSMEAN(j)

i/j	1	2	3	4	5	6
1	.	0.3124	0.2805	0.1205	0.1718	0.6015
2	0.3124	.	0.6041	0.2864	0.0501	0.1370
3	0.2805	0.6041	.	0.6476	0.0800	0.1833
4	0.1205	0.2864	0.6476	.	0.0367	0.0768
5	0.1718	0.0501	0.0800	0.0367	.	0.3225
6	0.6015	0.1370	0.1833	0.0768	0.3225	.

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.